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Chlorine Dioxide Disinfection and Granular Activated Carbon Adsorption

Evansville Waterworks Dept., IN

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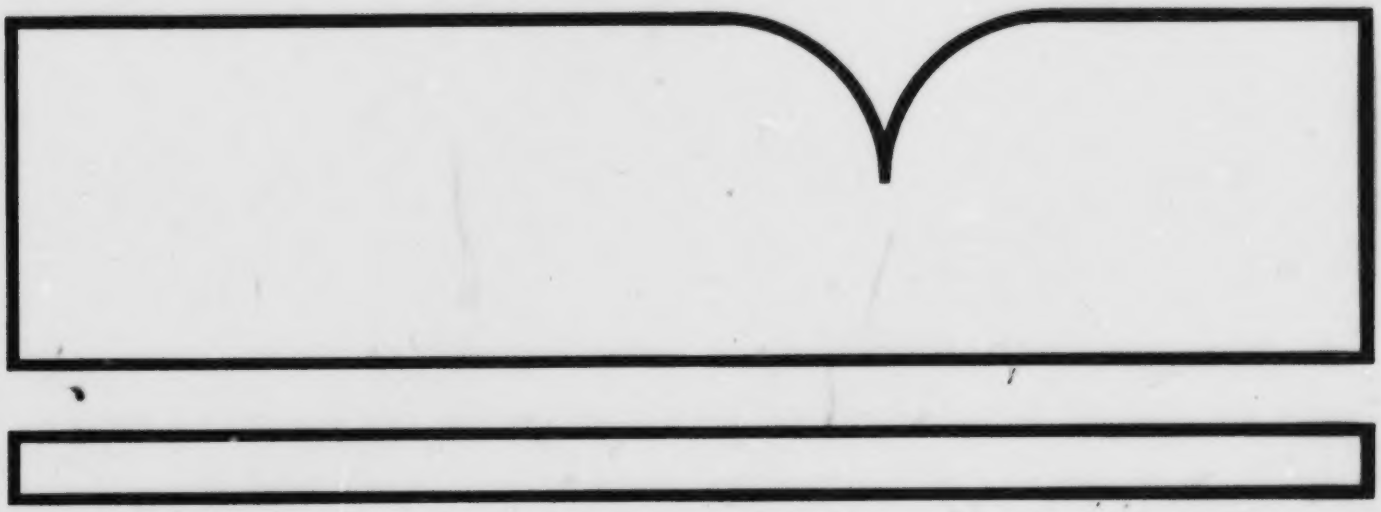

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CHLORINE DIOXIDE DISINFECTION AND GRANULAR ACTIVATED CARBON ADSORPTION

by

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Cooperative Agreement No. CR804902

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16. ABSTRACT

This research study was designed to evaluate chlorine dioxide disinfection as an alternative for drastically reducing or preventing the production of trihalomethanes that result during chlorination. Also, the effectivenss of virgin and reactivated granular activated carbon (GAC) for removal of organic compounds present in the source water as well as any formed after disinfection was investigated.

The performance of 0.38 m^3/minute (100 gallon per minute) pilot plant with pre and post chlorine dioxide disinfection and two parallel post-adsorber GAC contactors was compared to a full-scale plant using chlorine disinfection without GAC adsorption. The parallel GAC contactors consisted of virgin in one contactor and reactivated GAC in the other one that were continuously operated and evaluated until exhaustion. After about 90 days of operation, the GAC was educted and reactivated off-site by an infrared furnace.

Analysis performed during the project consisted of quantification of fourteen volatile and eight extractable organic compounds along with qualitative (detected/non-deteced) determinations by mass spec scans of 32 additional volatiles and 54 extractable organics. Additional data were collected on nine inorganic metals, TOC, and other parameters such as turbidity, SPC and total coliforms.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communication link between the researcher and the user community.

This report presents the results of a research effort to evaluate the use of chlorine dioxide disinfection in a pilot plant as compared with chlorine disinfection in a full-scale plant. The production and removal of trihalomethanes and specific organics are examined along with the effectiveness of granular activated carbon post adsorption.

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Director,
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Laboratory

ABSTRACT

This research study was designed to evaluate chlorine dioxide disinfection as a viable alternative to chlorine for drastically reducing or preventing the production of trihalomethanes (THMs). Also, the effectiveness of virgin and reactivated granular activated carbon (GAC) for removal of organic compounds present in the source water as well as any formed after disinfection was investigated.

The performance of a 0.38 m^3/minute (100 gallons per minute) pilot plant with pre and post chlorine dioxide disinfection and two identical parallel post-adsorber GAC contactors was compared to a full-scale plant using chlorine disinfection without GAC adsorption. The parallel GAC contactors consisted of virgin and subsequent reactivated GAC that were continuously operated and evaluated until exhaustion. After about 90 days of operation, the GAC was educted and reactivated off-site by an infrared furnace.

Analyses consisted of quantification of fourteen volatile and eight extractable organic compounds along with qualitative (detected/non-detected) determinations by mass spectrometer scans of 32 additional volatiles and 54 extractable organics. Additional data were collected on nine inorganic metals having regulated maximum contaminant levels, total organic carbon (TOC) and other parameters such as turbidity, bacterial standard plate count (SPC), and total coliforms.

Chlorine dioxide was an effective disinfectant that controlled the production of trihalomethanes and did not produce any organic by-products other than those noted with chlorine disinfection when looking at the priority pollutants. The two GAC contactors performed similarly with reactivation frequency determined by TOC and THM formation potential. Characterization of the GAC after exhaustion and reactivation showed that the carbon was essentially restored to the virgin state.

This report was submitted in fulfillment of Cooperative Agreement No. CR804902 by the city of Evansville, Indiana under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1976 to April 24, 1981. Work was completed as of November 1, 1981.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

GAC	-	granular activated carbon
MCL	-	maximum contaminant level
gpm	-	gallons per minute
m^3/day	-	cubic meters per day
MGD	-	million gallons per day
mg/L	-	milligrams per liter
LPS/sq. ft.	-	liters per second per square foot
ug/L	-	micrograms per liter
I	-	instantaneous
S	-	stored
MSSCV	-	mass spectrometer scan confirmation of volatile organics
MSSCE	-	mass spectrometer scan confirmation of extractable organics
NTU	-	nephelometric turbidity units
D	-	detected
ND	-	not detected
KWH/lb	-	kilowatt hours per pound
m^2/g	-	square meters per gram
EBCT	-	empty bed contact time
InstTHM	-	instantaneous trihalomethane concentration
TermTHM	-	terminal trihalomethane concentration
THMFP	-	trihalomethane formation potential

ACKNOWLEDGMENTS

The cooperation of the officials and waterworks employees at Evansville, Indiana is gratefully acknowledged. Special appreciation is extended to the Water Board for their understanding and timely response to various administrative matters.

Special appreciation is also extended to the Olin Corporation for supplying a chlorine dioxide generator and all related chemicals. Valuable guidance was provided by Robert Miller, Health Effects Research Laboratory, U.S. Environmental Protection Agency in analyzing for chlorine dioxide and its species.

This research project was a cooperative effort with technical assistance provided by Ben Lykins and Jack DeMarco of U. S. EPA's Municipal Environmental Research Laboratory.

SECTION 1

INTRODUCTION

Pursuant to provisions of the Safe Drinking Water Act (Public Law 93-523), the U. S. Environmental Protection Agency (U.S. EPA) designed extramural research to satisfy a basic need within the water treatment and supply industry: reduction or prevention of organic compounds in drinking water.[1] In conjunction with this research objective, an experimental study was initiated in Evansille, Indiana with the program being funded jointly by the Evansville Waterworks Department and the U.S.EPA.

In late 1974, Evansville waterworks officials were informed of U.S. EPA findings of minute amounts of bis (2-chloroethyl) ether and bis (2-chloroisopropyl) ether both in Evansville's raw and treated water. Because of these findings, Evansville accepted an opportunity to initiate a study for the removal of trace organics in its drinking water. The study was designed to provide insight on the development of a treatment method that would prevent or sharply deter the production of trihalomethanes in the disinfection process in addition to removing other organic compounds by adsorption on granular activated carbon (GAC). Specific objectives established for this project included:

- development of a water treatment process using chlorine dioxide as a disinfectant to evaluate the resultant production of trihalomethanes as compared to a process using chlorine disinfection.

- determining if any organic by-products are formed when using chlorine dioxide as a disinfectant as contrasted to chlorine disinfection.

- determining the disinfection efficiency of chlorine dioxide and its capability of providing a residual necessary for full-scale distribution use.

- determining the effectiveness of virgin and subsequently reactivated GAC for removal of organic compounds present in the filtered water, as well as any formed after chlorine dioxide disinfection.

SECTION 2

CONCLUSIONS

Evaluation of chlorine dioxide disinfection and GAC treatment in a 0.38 m^3/min (100 gpm) pilot plant have provided some insight into this treatment scheme. A comparison of the addition of chlorine dioxide and chlorine to the raw water showed that both disinfectants provided similar disinfection qualities through conventional treatment. Also, because of the strong oxidative properties of chlorine dioxide and a lesser demand, a lower mass dose was sufficient to produce effective disinfection as compared to chlorine. By using a lower dose of chlorine dioxide, some of the difference between the cost of chlorine dioxide and chlorine can in part be compensated.

Application of chlorine dioxide to the raw water produced less terminal THM in the finished water than chlorine addition (for all runs an average of 51 ug/L with chlorine dioxide addition and 130 ug/L with chlorine). The finished water was stored for three days with a chlorine residual to produce the Term THM. Also in this study, chlorine dioxide disinfection did not produce any organic byproducts other than those noted with chlorine disinfection when looking at the priority pollutants. Consequently, the GAC was lightly loaded with specific organic constituents.

Spent GAC was subsequently reactivated three times and essentially restored to virgin state as indicated by several GAC properties and performance comparisons to virgin GAC. Losses incurred during GAC reactivation were about 5 percent with overall system losses (eduction, handling, transport and reactivation) averaging about 8 percent.

Production of chlorine dioxide did not proceed stoichiometrically thereby introducing some chlorite and chlorine. Both chlorine and chlorine dioxide were effectively removed by the GAC and the chlorite was partially removed.

The use of chlorine dioxide as the primary raw water disinfectant is a viable alternative to chlorine disinfection in some situations for reducing the trihalomethane concentrations to meet promulgated drinking water standards.

SECTION 3

RECOMMENDATIONS

1. Comprehensive health effects studies should be undertaken to evaluate the extended use of chlorine dioxide as an alternative to chlorine for drinking water disinfection.

2. The production of chlorine dioxide needs improvement. Although several methods are available by various manufacturers, work needs to be done on improving these procedures so that less and preferably no chlorite or chlorine is produced.

3. An analytical method for the determination of chlorate that can be used effectively by waterworks chemist needs to be developed.

4. Use of chlorine dioxide only as a raw water disinfectant should be considered for reduction of trihalomethane concentrations at Evansville, Indiana, after applying the residual oxidant recommendations stated in the trihalomethane regulations.

SECTION 4

TREATMENT PLANT DESIGN AND OPERATION

Full-Scale Treatment Plant

The Evansville Waterworks Filtration Plant was used as the control for this study. The plant is located on the Ohio River about one mile upstream from the city of Evansville. It consists of two separate treatment systems, each having a hydraulic capacity of approximately 1.14×10^5 m^3/day (30 MGD). The South Plant was used as the control because of construction activity in the North Plant. Also, since the overall retention time of water in the South Plant is considerably less than that of the North Plant, using this system enabled waterworks personnel to easily sample the same portion of water after various phases of treatment. This procedure was utilized to help eliminate any inconsistencies in sample data because of daily fluctuations in the source water.

The South Plant (see Figure 1) consists of two primary settling basins, two secondary settling basins, and eight rapid sand filters. Each primary settling basin is 39.6 meters (130 feet) in diameter and 5.3 meters (17.5 feet) deep with a capacity of approximately 6,813 m^3 (1.8 million gallons). The secondary settling basins are each 27.4 meters (90 feet) in diameter with a 4.6 meter (15-foot) sidewall depth and a capacity of 2,744 m^3 (0.725 million gallons).

Water from the secondary settling basins enters the South filter building through concrete-lined steel pipes to eight rapid sand filters consisting of media from top to bottom of:

15.2 centimeters (6") anthracite

55.5 centimeters (22") fine sand

10.2 centimeters (4") coarse sand

7.6 centimeters (3") fine gravel

7.6 centimeters (3") medium gravel

10.2 centimeters (4") coarse gravel

Chlorine and alum were added before primary settling with average concentrations of 6 and 28 mg/L, respectively. These dosages varied depending on the demand and turbidity of the raw water. A free chlorine residual of 1.5-2.0 mg/L was maintained after sand filtration with any make-up chlorine being added before the water passed into a common clearwell. Approximately 12 mg/L of lime was added after primary settling for pH adjustment to 8.0 and about 1.5 mg/L of fluoride was added immediately before the rapid sand filters.

Pilot Plant

To avoid disrupting normal operating procedures at Evansville, a 0.38m^3/minute (100 gpm) Neptune Micro-Floc unit was purchased for the study and housed on-site. River water was supplied to this unit by approximately 189 meters (620 feet) of 10 cm (4 inch) PVC pipe. The raw water was disinfected and then treated with alum and polymer for turbidity removal. This chemically treated water was mixed, flocculated, and then clarified in a settling tube chamber. Clarified water then entered a mixed media filter chamber and passed through a filter bed to an underdrain system where it was pumped to two parallel GAC contactors or directly to a combination clearwell and backwash tank (Figure 2). The flow utilized in the pilot plant was 0.30 m^3/min (80 GPM) with a relatively short detention time of approximately 37 minutes.

Disinfection with chlorine was achieved by using a 3% sodium hypochlorite (NaOCl) solution, whereas chlorine dioxide was produced using an Olin generator. With this generator, sodium hypochlorite (NaOCl) was reacted with sodium chlorite ($NaClO_2$) after the pH of the reaction had been adjusted to 3.0$\pm$0.5 with hydrochloric acid (HCL). Average alum and polymer dosages of 12 and 0.8 mg/L respectively were used for turbidity removal. The polymer used for this project was an anionic high molecular weight flocculant, Nalcolyte 8172. Although it was not used in the full-size plant, the short detention time of the water in the pilot plant made the use of polymer necessary. For pH control to about 8.0 an average lime dosage of approximately 6.0 mg/L was added to the settling tube effluent.

The GAC contactors and clearwell were especially constructed for this project and the inside of each was treated with a non-toxic and chemical resistant epoxy paint to control corrosion. The paint used for this protective treatment was Glidden's "Glid Guard" No. 5250 and 5452 (FDA No. 1753000). No extensive testing was done to evaluate the paint for leaching of organic contaminants. However, during the study, no organics were detected in the GAC effluent that were not in the influent.

The design and operating parameters for the pilot plant that were used in this study consisted of:

Rapid mix chamber - volume of 1.1 cubic meters (39 cu. ft.)

Flocculator - volume of 3.4 cubic meters (120 cu. ft.)

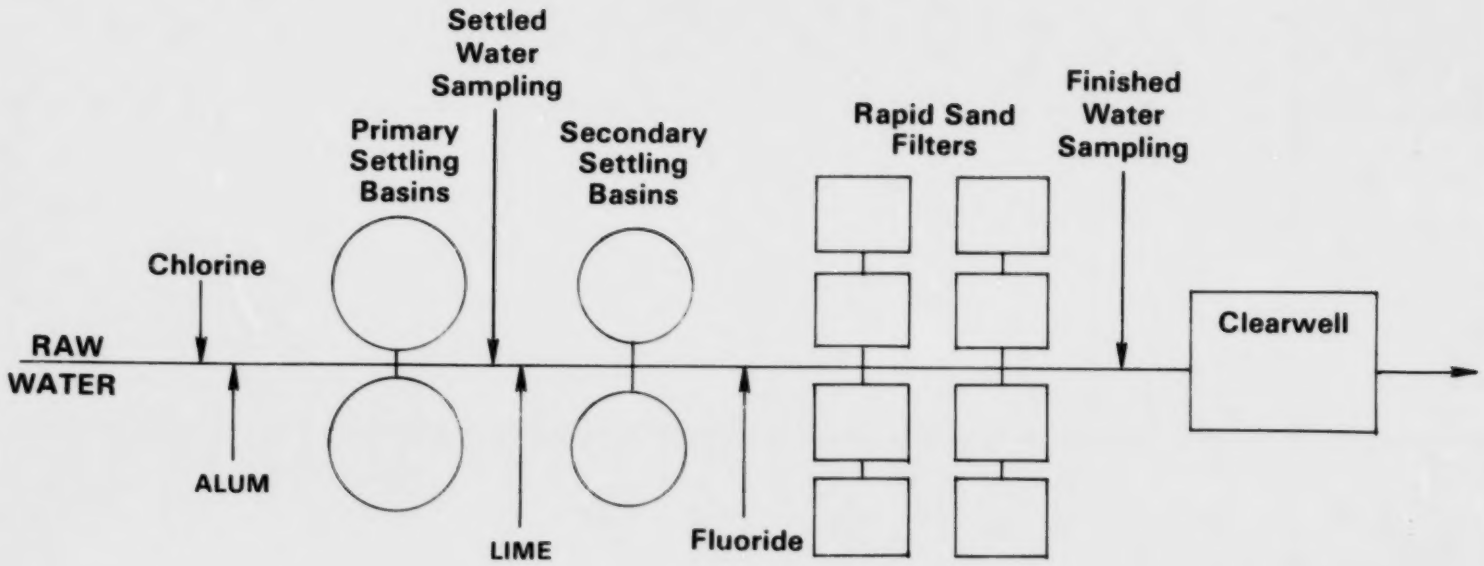

FIGURE 1. FLOW DIAGRAM OF EVANSVILLE, INDIANA FULL-SCALE SOUTH PLANT.

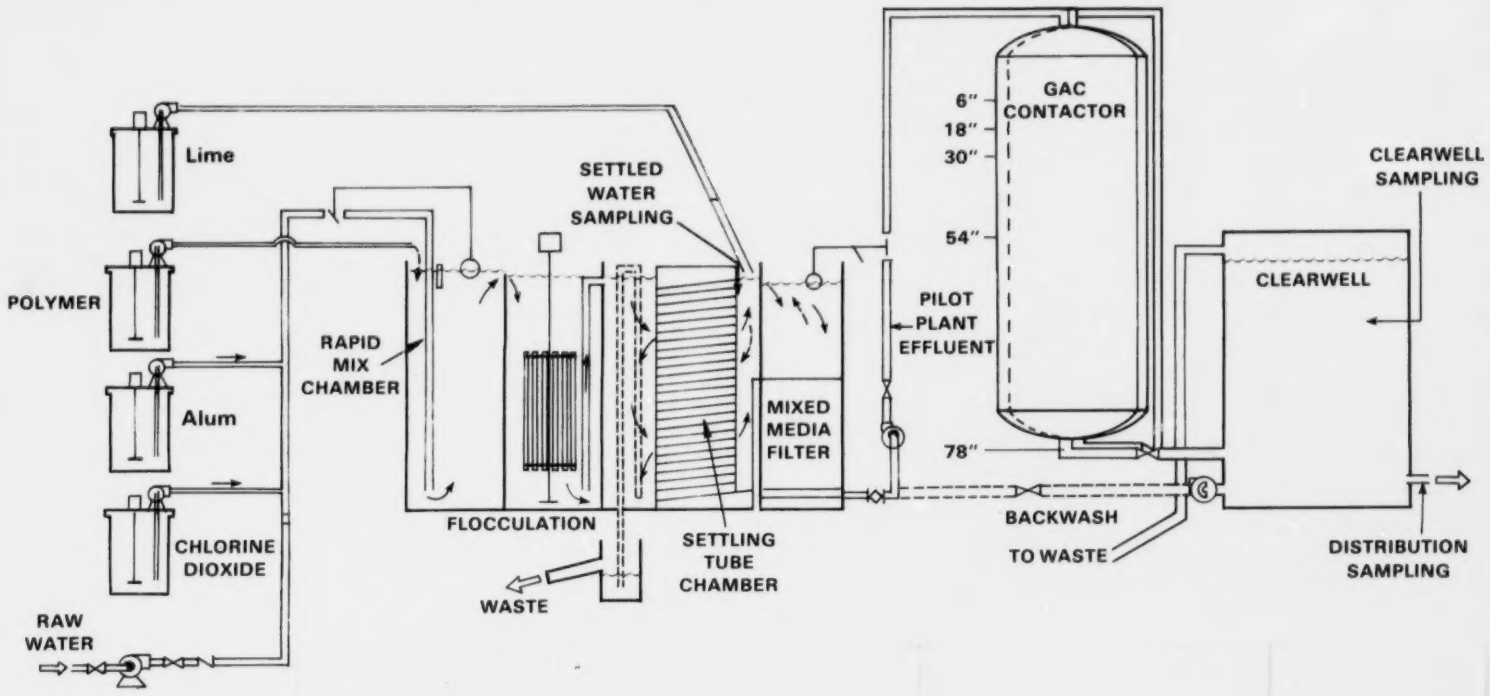

FIGURE 2. SCHEMATIC DIAGRAM OF EVANSVILLE, INDIANA PILOT PLANT.

Tube settler - volume of 4.2 cubic meters (150 cu. ft.)

Mixed media filter - media of sand with garnet and anthracite, 1.9 square meters (20 sq. ft.) of filter area. Backwash of the mixed media filter was performed manually or automatically by using a headloss vacuum switch.

GAC contactors (2 pressure) - each constructed with a straight column height of 2.7 meters (9.0 feet) and an inside diameter of 0.97 meters (38 inches). An average GAC bed depth of 2.0 meters (6.5 feet) was used to allow for GAC expansion during backwash. A hydraulic loading of 12.2 m/hour (5.1 gpm/sq.ft.) provided an empty bed contact time of 7.7 minutes per contactor during short-term preliminary runs. A contact time of 9.6 minutes was used in the long term runs. Sample taps constructed of 0.6 cm (1/4 inch) diameter stainless steel pipe were provided at one-foot increments. Carbon was supported on a Neva Clog underdrain with a 10 cm (4 inch) diameter opening located just above the carbon support for GAC eduction. A similar 10 cm (4 inch) opening at the top of each contactor permitted easy carbon replenishment.

Clearwell - volume of 17.0 m^3 (600 cu. ft.) above grade steel tank with a useable capacity of 16,987 liters (4,488 gallons). This also served as the source for filter backwash water.

Reservoir - iron water pipe 11 meters (36 ft.) long and 5.6 cm. (2.25 inches) in diameter connected to the clearwell to simulate drinking water retention at a dead-end in the distribution system.

SECTION 5

SAMPLING AND ANALYSIS

Sample Collection

All samples for the project were collected by Evansville laboratory personnel on a time-sequence basis. As mentioned previously in the full-scale plant description, this procedure was utilized to help eliminate any inconsistencies that might occur because of daily fluctuations of various parameters in the source water.

By calculating the volume and capacity of the different settling basins of the South Plant and by considering the current rate of pumpage, the approximate detention time at various locations in this treatment system was determined. It must be noted that this method of calculation assumes complete mixing of water throughout the treatment plant and does not allow for the obvious possibility of water "short circuiting" across the top of a settling basin while other water remains relatively stationary.

For example, given the following infomation, the various sampling times for the full-scale plant could be determined.

Initial raw water sampling: 8:00 a.m.

Pumpage rate (South Plant): 7.6×10 m^3/day; 20 MGD

Primary Settling basins: 6,813 m^3; 1.8 MG (each)

Secondary settling basins: 2,744 m^3; 0.725 MG (each)

20 MGD $\div$ 24 Hrs. = 0.8333 million gallons per hour (MGH)

Sampling after initial coagulation and settling:

3.6 MG (both primary basins) $\div$ 0.8333 MGH = 4.32 hours.

Sampling time = 12:19 p.m.

Finished water sampling:

5.05 MG (primary and secondary basins) $\div$ 0.8333 MGH = 6.06 hours.

Sampling time = 2:04 p.m.

Because the amount of time that water was detained in any other locations in the South Plant was minimal, only the detention periods of the settling basins were used to determine specific sampling intervals. This procedure was used throughout the project to maintain consistency.

The specific sampling times for various locations in the pilot plant were calculated in much the same way. The overall detention time of the Micro-Floc unit was approximately thirty-seven minutes with the GAC contactors having an estimated detention time of 12 minutes (not to be confused with EBCT). To obtain a more representative sample in the pilot plant clearwell, samples were taken from approximately two feet below the surface of the water. The detention time at this depth was estimated to be about thirty minutes. By utilizing these figures, the following sampling sequence was employed in the pilot plant:

8:00 a.m. - Initial sampling (raw water)

8:25 a.m. - Settled water sampling

8:37 a.m. - Sampling of Micro-floc effluent

8:40 a.m. - Earliest contactor sampling

8:45 a.m. - Mid-point contactor sampling

8:50 a.m. - Contactor effluent sampling

9:20 a.m. - Clearwell sample.

Sampling locations in the full-scale plant were chosen that would best coincide with the sampling locations in the pilot plant. Because of the differences of the two treatment systems, a sampling point after initial coagulation and settling and one from the South Plant effluent were considered to be the only pertinent locations. These two sampling points would correspond to the settled water location in the pilot plant and the pilot plant effluent (GAC influent). Only one raw water sample was collected from the feed system to both plants.

The various locations for sampling in the pilot plant were selected to provide an in-depth evaluation of every step in the treatment process. The pilot plant sampling points utilized are listed below:

1. Raw water

2. Settled water

3. Pilot plant effluent

4. GAC contactor [15.2 cm (6"), 45.7 cm. (18"), 76.2 cm. (30")] for short-term runs.

   [76.2 cm. (30"), 137.2 cm. (54"), 198.1 cm. (78")] for long-term runs

5. GAC contactor effluents [After 198.1 cm (78 in.)]

6. Pilot Plant clearwell

7. Simulated Pilot Plant distribution effluent

Because of the increased lengths of the long-term runs, and since breakthrough was observed at the lesser bed depths during the experimental modes, the GAC contactor sampling locations were changed to 76.2 cm. (30"), 137.2 cm. (54") and 198.1 cm. (78") prior to the initiation of the three month runs. The need for this change and a discussion of the observed breakthrough will be presented later in this report.

Sample Analyses

A wide range of analyses were performed on various samples collected from both treatment plants. The bacteriological (B), pH, turbidity, chlorine, chlorine dioxide (R), and wet chemistry (WC-Fe and Mn) analyses of these samples were performed by the laboratory personnel at the Evansville plant. The other analyses were performed under a contractural agreement with the Radian Corporation's California Analytical Laboratory.

The initial analyses consisted of the following volatile and extractable organic compounds:

Instantaneous (I)

[Quantification of seven volatile organic compounds]

chloroform	carbon tetrachloride
bromodichloromethane	1,2 - dichloroethane
dibromochloromethane	tetrachloroethylene
bromoform	

In addition, qualitative (detected/non-detected) determinations were performed on 32 additional volatile organic compounds (MSSCV - mass spec scan confirmation of volatiles). The detection limit for all of the instantaneous compounds was 0.1 ug/L except for bromoform which was 0.2 ug/L.

[Quantification of fourteen extractable organic compounds (E)]

hexachlorobenzene	2,4,5 - TP (silvex)
hexachloroethane	aldrin
xylene	endrin
2,4 - D	lindane

methoxychlor	DDT
toxaphene	chlordane
dieldrin	heptachlor

Also, 54 additional extractable organic compounds were qualitatively determined, detected/non-detected (MSSCE - mass spec scan confirmation of extractables). The detection limit for all of the extractable compounds was 0.1 ug/L.

[Quantification of Inorganic Compounds (MCL)]

Presented below are the nine inorganic compounds regulated with an MCL that were analyzed along with their respective detection limits.

Arsenic (0.01 mg/L)	Mercury (0.0005 mg/L)
Barium (0.1 mg/L)	Selenium (0.005 mg/L)
Cadmium (0.01 mg/L)	Silver (0.05 mg/L)
Chromium (0.05 mg/L)	Nitrate (0.05 mg/L)
Lead (0.02 mg/L)	

[Total Organic Carbon (TOC)]

Terminal Samples

All samples designated (S) were analyzed for terminal trihalomethane concentrations after being stored for a period of 72 hours. These samples were stored in 270 mL bottles containing a sufficient amount of chlorine or chlorine dioxide so as to maintain a residual. The samples also contained a buffer to maintain a pH representative of the water entering the distribution system and were stored at ambient temperature representative of the water in the distribution system. At the end of 72 hours, the temperature and pH of the samples were checked and the samples were analyzed to confirm that a residual still existed. Forty milliliter portions of these samples were then sent to the contract laboratory for analyses of the seven volatile compounds noted previously.

After reviewing the data from the experimental modes of operation, a number of changes in the analyses for the long-term run were instituted. Because many of the substances originally analyzed for quantification were never detected, other detected compounds were selected for quantification with the remaining compounds qualitatively analyzed. The alterations made in the analyses for the long-term phase of the project are listed below.

The following substances were added to the volatile group for quantitative analysis:

trichloroethylene	ethylbenzene
1,1 - dichloroethylene	acrolein
1,1,1 - trichloroethane	acrilonitrile
benzene	

These compounds were added to the extractable group for quantitative analysis:

1,2,4 trichlorobenzene	1,2 dichlorobenzene
bis (2-ethyl hexyl) phthalate	1,4 dichlorobenzene
butyl benzyl phthalate	hexachlorobenzene
di-N-butyl phthalate	hexachloroethane

The quantification of the fourteen extractable compounds in the original test modes was eliminated completely and the following compounds from that group were included in the MSSCE for qualitative analysis only:

aldrin	heptachlor
dieldrin	methoxychlor
chlordane	lindane
4,4 - DDT	toxaphene
endrin	

Analytical Equipment and Procedures

Samples analyzed in the Evansville Waterworks laboratory were run by plant personnel using the following methods:

Turbidity

Nephelometric Method run on an HF Instruments Model DRT 100 Turbidimeter. Instrument was standarized prior to each set of tests with a 0.14 NTU Standard and checked quarterly with freshly prepared 1,10,100 and 1000 NTU Formazin Solutions.

Chlorine

A Fisher Cl Titrimeter, Model 393, was used to determine the free chlorine by the Amperometric Titration Method.

Chlorine Dioxide

A La Motte-Palin DFD-FAS Titrimetric Unit, Model DT, and the Olin Water Service Chlorophenol Red (CPR) Method were used to determine ClO_2 residuals. The La Motte-Palin Method[2] was also used to determine free chlorine and chlorite residuals in the pilot plant.

pH

An Orion Ionalyzer, Model 407A, with an Orion Research Model 91-04-01 combination electrode were used for pH measurement. The instrument was standardized using pH 7 and 10 buffers.

Temperature

A standard mercury thermometer, with a range of -20°C to 110°C with 1°C increments, was used to obtain all temperatures.

Iron

The Hach 2, 2-bipyridine Method was used with the results read on Bausch and Lomb Spec 20 at 512.5 nm. The test and instrument were checked for accuracy using various concentrations of a standard iron solution.

Manganese

The Hach Persulfate Method, using Manganese Solution, Ammonium Persulfate, and heat, was used to determine the manganese concentration with results read on a Spec 20 at 525 nm. The test and instrument were checked for accuracy using various concentrations of a standard manganese solution.

Total Coliforms

The membrane filter method was used for all determinations of total coliforms. A sterile Millipore Pyrex glass filtering apparatus was used along with Millipore presterilized filters. The filters were type HCWG, 47 mm, with a pore size of 0.7 um. Presterilized Millipore media pads and Gelman plastic, 50 mm x 9 mm, Petri dishes were used. The media was Difco M Endo Broth MF. Raw water samples were diluted so that 1 mL, 0.1 mL, and 0.01 mL were filtered. Blanks were run before and after each sample series using sterile buffer water and sterile filters. The buffer water, 1.2 mL Phosphate buffer/liter distilled water, was used for dilution and rinse purposes. All samples were incubated at 35°C for 24 hours. Every positive coliform colony on a finished water sample was checked by the Presumptive and Confirmed Multiple-Tube Fermentation Technique. The media used for the Presumtive test was Difco Lauryl Tryptose Broth, and Difco Brilliant Green Bile 2% was used for the confirmed test. The Lauryl Tryptose Broth was also used to check the sterility of one from each set of prepared sample bottles.

Standard Plate Count

The Standard Plate Count procedure outlined in the 14th edition of Standard Methods was followed. Twenty five milliliters of BBL Standard Methods Agar (Tryptone Glucose Yeast Agar) was used in each plate. Appropriate dilutions of 1:10 or 1:100 were made for samples taken from the raw water, settled water and carbon contactor effluent. One milliliter of these dilutions and of all other samples were plated. Duplicate plates were prepared for each sample or sample dilution. A control plate was poured for each series of samples to check the sterility of the media plates and the dilution water. All plates were incubated at 35°C for 48 hours. All bacterial counts were reported as the Standard Plate Count per milliliter.

The analytical procedures used by the Radian Corporation for analyses of the Evansville samples consisted of the following:

Instantaneous and Stored Volatile Organics (I/S)

The sample purging system consisted of a 40 mL purging device, and eight inch Tenax trap (Supelco, Inc.) for adsorption/desorption and a six port stainless valve (Valco, Inc) for controlling flow directions. The chromatographic system utilized was a Varian 3700 equipped with a dual Coulson Electrolytic Conductivity Detectors (Western Scientific, Inc.). The chromatographic column was a 2 m. by 2 mm. i.d. glass column packed with 0.2% Carbowax 1500 on Carbopak C. The initial chromatographic temperature was 50°C which was held for five minutes, then programmed at 8°C to 160°C and held until tetrachloroethylene eluted. A 20 mL sample aliquot was used. It was purged for 17 minutes and then the valve was switched so that the adsorbed purgable organics were thermally desorbed for 5 minutes onto the head of the gas chromatographic column.

Mass Spec Scan Confirmation of Volatile Organics (MSSCV)

The same type of purging system and chromatographic parameters were used for this group as described above for the I/S samples with the exception of the purging vessel which was larger, thereby permitting use of the entire 40 mL sample for analysis. The purge time was also longer at 25 minutes. In addition, two internal standards, dichlorobromomethane for early eluting pollutants and 1,4-dichlorobutane for late eluting pollutants were added to approximately 0.5 ug/L concentration. The appropriate ratio of pollutant/internal standard was calculated for pollutants found in the sample. These ratios could then be compared directly to the standard ratios. When the sample ratio was larger, the pollutant was reported as detected (D). Conversely, when the ratio was lower, the compound was reported as not detectable (N/D).

Extractable Organics

The (E) samples were extracted using 15 percent methylene chloride in hexane after acidification of a two liter aliquot. This concentration step effectively eliminated the methylene chloride leaving only the hexane solvent. After concentration, the hexane was methylated using diazomethane in ethyl ether. The sample was then further concentrated to 5 mL. Two analyses were run on this fraction. The first analyses was for hexachloroethane and bis (2-chloroethyl) ether which was done by GC/MS/DS with the data collected by selected ion monitoring in order to achieve adequate sensitivity. Next, the methylated chlorophenoxy herbicides and neutral pesticides were analyzed by electron capture gas chromatography on a Varian 3700 equipped with dual, linearized electron capture detectors. A short temperature program from 160°C to 200°C was used. The chromatographic column was the typical mixed phase pesticide column, 1.5/1.95% Sp-2250/SP2401, 2 meters long by 2 millimeters i.d. In both analyses, synthetic standards were used that represented 0.1 ug/L in concentration of each pollutant at 100 percent recovery.

Mass Spec Scan Confirmation of Extractables (MSSCE)

With this group, a four liter sample aliquot was used for extraction with methylene chloride. The same analytical approach was used as in the MSSCV analysis. A standard, prepared by diluting the U.S. EPA priority pollutant standard to an equivalent of 0.1 ug/L was injected directly into the GC/MS. Both sample concentrate and standard contained d_{10} anthracene. The appropriate ratios were calculated, and comparison of sample and standard ratios produced the "D" or "N/D" reported. Qualitative analyses were performed by subtracting a background mass spectrum from a spectrum selected at a peak apex and then subjecting the resulting spectrum to the Finnigan library for comparison.

Inorganic Compounds (MCL)

The MCL samples were collected in one-quart polyethylene bottles and were preserved with HNO_3 to a pH <2. Sample preparation and appropriate digestion procedures were performed according to the U.S. EPA manual of Methods for the Chemical Analysis of Water and Wastes (1974). The only exception to the above was that arsenic and selenium analyses were completed using $NaBH_4$ instead of $SnCl_2/Zn$ slurry as stated in the above referenced methods. The instrumentation used for these analyses was a Perkin-Elmer Model 603 Atomic Absorption Spectrophotometer.

Nitrates

For nitrates, a clarified sample was adjusted to between pH 5 and 9 before 75 mL of an ammonium chloride/EDTA reagent was added to 25 mL of the sample or diluted aliquot. This solution was mixed and placed on a cadmium column (1 cm. ID x 30 cm. with a 100 mL reservoir)

with the flow adjusted by means of a pinch clamp to approximately 5 mL/min. The first 25 mL from the column were discarded with the remainder collected. To 50 mL of reduction column eluate was added 2 mL of color reagent and mixed. The absorbance was measured in 1 cm. tubes at 540 nm on a Turner Model 300 Spectrophotometer with a 1 cm. light path between 10 minutes and 2 hours.

Total Organic Carbon (TOC)

TOC samples were collected in 4 oz. glass bottles with teflon-lined screw caps. No preservatives were added but the temperature of the sample was maintained at 4°C until prepared for analysis. Samples were run on a Dohrmann DC-54 Low Level TOC Analyzer with a POC-2 sparger that was designed to handle particulates up to 0.5 mm in diameter. Using syringes, ten mL of sample and 0.5 mL of oxidant (5 gm. of potassium persulfate and 3 mL of phosphoric acid in 100 mL of distilled water) were added to the POC sparger. The mixture was purged with helium at 120 mL per minute for 3 minutes to remove purgeable organics. At the same time, the non-purgeable organics were trapped by a LiOH scrubber. These organics were converted to methane and measured quantitatively with a flame ionization detector and displayed digitally. The values reported were the mean of duplicate analyses.

Those samples that were shipped to the contractual laboratory were placed in appropriate containers supplied by the contractor. All volatile samples were shipped head-space-free. The I, S, and MSSCV sample were placed in 40 mL glass vials containing sodium thiosulfate. The caps used on these vials were teflon-lined. The extractable samples were placed in one-quart glass bottles that contained no additives. MSSCE samples were shipped in one-gallon glass bottles containing methylene chloride and TOC samples in 4 oz. glass vials containing no preservative. All of the MCL samples except the nitrates were shipped in one-quart plastic bottles containing 5 mL of concentrated nitric acid. The nitrate samples were shipped in 8 oz. glass bottles with 0.5 mL of concentrated sulfuric acid.

Quality Assurance

The quality assurance procedures practiced by Evansville were presented earlier in the Analytical Equipment and Procedures section. Those procedures utilized by the Radian Corporation are outlined below:

Instantaneous and Stored Volatiles (I/S)

1. The gas chromatograph was calibrated daily using standards at three concentrations - usually 0.5 ug/L, 2 ug/L, and 20 ug/L. Fewer standards were used only when the instrument had been used recently and had exhibited good stability.

2. System blanks were run between the calibration standards and the samples, and after any sample that showed significant amounts of the compounds of interest.

3. Synthetically prepared ("spiked") samples were submitted to each laboratory by the quality assurance officer at Radian as part of their independent blind sample audit program. The frequency of these samples varied based on the quality of the data for previous samples - the better the results the fewer samples were run. Previous results from the contract laboratory had been well within acceptable limits, and therefore synthetic samples were run on a relatively infrequent basis.

Mass Spec Scan Confirmation (MSCCE/MSSCV)

1. The mass spectrometer was calibrated daily to ensure proper spectral mass assignment.

2. The chromatographic system was calibrated by injection of two analytical standards, containing the compounds of interest at the equivalent of 0.2 and 2 ug/L. This procedure insured, on a daily basis, both proper sensitivity for analyses of the compounds of interst and quantitative accuracy from a concentration range of near the detection limit to approximately 10 ug/L. (This concentration range covered the range of interest for all the compounds being analyzed.)

3. With each set of extractable samples, a method blank was prepared and analyzed. This method blank consisted of organic free water (deionized and distilled) extracted and analyzed just as the samples. Using the method blank allows compensation for background concentrations of the compounds of interest.

4. For each volatile sample, a laboratory blank was analyzed immediately prior to the analysis of the sample. This allowed for compensation because of background, particularly methylene chloride and chloroform. In cases where the methylene chloride, chloroform, or other contaminants were at sufficient levels so as to interfere (i.e., 1 ug/L) the analysis of samples was not initiated until the problem was solved.

Maximum Contaminant Level of Inorganic Compounds (MCL)

1. The analytical instrumentation for metals analyses was calibrated using a blank and three standards.

2. An EPA Quality Control check standard of known concentration was run to confirm the calibration.

3. Blind check samples were analyzed and indicated the accuracy of the method to be within $\pm$ 20 percent.

Nitrates

Nitrate analysis was performed by the cadmium reduction column method. Calibration of the method involved the preparation of a five (5) point calibration curve. With each set of samples at least one blank and one duplicate were analyzed. Independent, blind check samples indicated the accuracy of the method to be within ± 10 percent.

Total Organic Carbon (TOC)

The Dohrmann DC-54 TOC instrument was calibrated every four hours with a potassium hydrogen phthalate standard. Each sample was analyzed in triplicate and the average of the two closest results was retained. This process was repeated twice and the average of the two results was the number that was reported. Thus, each data point reported represented an average of four (4) separate determinations. In addition, blind check samples were analyzed as part of Radian's independent corporation-wide QA program. These results indicated the TOC accuracy to be within ± 5 percent.

As a means of further assessing credibility in the results reported for this project, quality control samples supplied by U.S. EPA's Environmental Monitoring and Support Laboratory (EMSL) were analyzed by Evansville's analytical contractor. The methodology and instrumentation utilized for these samples were the same as presented previously.

The EMSL quality control samples consisted of volatile organics, pesticides, heavy metals, and TOC. Although the results reported for these samples seem to be within acceptable limits, comparison were also made to other laboratories. Data from four other laboratories was available for establishing a range for comparison of the various constituents in the volatile organic samples at two levels of concentration. As can be seen in Table 1, only three of the volatile organic compounds were outside of the range developed from data reported by the four laboratories. Only bromoform was outside the range at both concentration levels.

For comparison of heavy metals and TOC data, an estimation of acceptance limits at a 99 percent confidence interval developed by EMSL-Cincinnati from six distinct studies based on approximately fifty reported values for each parameter from a combination of EPA and State laboratories, were used. All of the data from these quality control samples submitted to Evansville's contractor was within the acceptance limits as shown in Table 2.

As with the heavy metals and TOC, the pesticides data were evaluated on the basis of 99 percent confidence limits established from approximately forty reported locations. Values for the quality control samples compared favorably with the true values and were well within the 99 percent confidence limits as seen in Table 3.

TABLE 1. QUALITY CONTROL VOLATILE ORGANICS COMPARISON

Parameter	True Value (ug/L)	Range (ug/L)	Evansville (ug/L)
Chloroform	9.13	5.3 - 12.2	8.6
	68.46	61 - 78.5	73
1,2 Dichloroethane	1.39	0.9 - 2.0	1.5
	27.21	25 - 38.8	21
Carbon Tetrachloride	1.68	0.9 - 1.8	1.2
	12.57	9.7 - 12.5	12
Bromodichloromethane	1.19	0.9 - 2.4	1.7
	11.90	13.8 - 19.9	14
Dibromochloromethane	2.74	1.8 - 2.6	2.3
	17.15	12.2 - 17.0	18
Bromoform	2.85	ND - 2.6	3.8
	14.24	ND - 15.8	16
Tetrachloroethylene	8.76	6.6 - 9.8	8.9

TABLE 2. QUALITY CONTROL HEAVY METAL AND TOC COMPARISON

Parameter		Sample 1 True Value	Sample 1 99% Conf. limit	Sample 1 Evans-ville	Sample 2 True Value	Sample 2 99% Conf. limit	Sample 2 Evans-ville	Sample 3 True Value	Sample 3 99% Conf. limit	Sample 3 Evans-ville
TOC	mg/L	7.3	5.3 - 10.1	7.3	---	---	---	---	---	---
Arsenic	ug/L	26	13 - 41	27	109	45 - 175	85	154	63 - 248	130
Cadmium	ug/L	5.2	1.1 - 9.7	9	23	14 - 31	23	73	49 - 89	79
Chromium	ug/L	16	1.6 - 31	30	154	94 - 204	158	209	131 - 273	204
Lead	ug/L	22	2.9 - 46	<20	298	193 - 396	360	352	230 - 465	390
Mercury	ug/L	0.80	0.16 - 1.46	0.61	4.5	ND - 8.1	7.2	9.4	ND - 16.9	10
Selenium	ug/L	5.2	1.9 - 9.1	6.0	26	4.8- 43	19.1	44	8.2 - 71	47

TABLE 3. QUALITY CONTROL PESTICIDE COMPARISON

Parameter		Sample 1 True Value	Sample 1 99% Conf. limit	Sample 1 Evans-ville	Sample 2 True Value	Sample 2 99% Conf. limit	Sample 2 Evans-ville
Heptachlor	ug/L	0.14	0.04 - 0.22	0.16	0.08	0.01 - 0.14	0.10
Aldrin	ug/L	0.28	ND - 0.61	0.22	0.15	ND - 0.28	0.14
DDE	ug/L	0.62	0.26 - 0.94	0.50	0.18	0.01 - 0.36	0.14
Dieldrin	ug/L	0.33	0.09 - 0.57	0.36	0.13	ND - 0.29	0.13
DDD	ug/L	0.62	0.21 - 1.02	0.56	0.17	ND - 0.44	0.14
DDT	ug/L	0.75	0.41 - 1.07	0.68	0.15	0.07 - 0.25	0.14
Chlordane	ug/L	2.77	ND - 6.56	2.4	0.79	ND - 1.64	0.75

SECTION 6

EXPERIMENTAL MODES OF OPERATION

The project at Evansville was designed to include four sequential phases of operation: training, shakedown, optimization, and long-term operating phase. The training and shakedown phases were included to assure efficient operation of the pilot plant and to establish reliable sampling technique. Since these two phases were not intended to produce useable sampling data, they will not be discussed further.

The optimization phase consisted of a control study and three different experimental modes of operation. For the control study, the pilot plant was operated for two weeks using pre (before coagulation and settling) and post (after mixed-media filtration) chlorine disinfection to allow a performance comparison to the full-scale plant. The other three experimental modes were three weeks in duration and were evaluated to determine which treatment method would be utilized during the long-term operating phase (Table 4). The results obtained and observations noted for each of the short-term modes of operation are presented below.

Run #1 (Control Study)

The pilot plant was utilized for a two-week evaluation without the carbon contactors in operation to determine if the full-scale plant could be used as a control for subsequent experimentation. This two-week study revealed, as shown in Table 5, that the average concentration of the two plant effluents were similar.

In addition to average values, the data for total instantaneous THMs and TOC were subjected to the "t-test" at a 95% confidence level. This test showed no significant difference for either parameter when data from the pilot plant were compared to the full-scale plant.

The close comparison between the two plants occurred even though their treatment systems were dissimilar. Because of a much shorter detention time in the pilot plant (approximately 37 minutes as opposed to a 5 hour detention time in the full-scale plant) an anionic high molecular weight flocculant was used to achieve an acceptable degree of turbidity removal. By using this flocculant, the major difference between the two treatment systems was offset and the performance of the pilot plant closely resembled that of the full-scale plant.

TABLE 4. EXPERIMENTAL MODES OF OPERATION FOR PILOT PLANT

Run	CHLORINE	CHLORINE DIOXIDE	ALUM	POLYMER	MIX	SETTLE	LIME	FILTER	CARBON	CHLORINE	CHLORINE DIOXIDE
1	X		X	X	X	X	X	X		X	
2	X		X	X	X	X	X	X	X	X	
3			X	X	X	X	X	X	X		X
4		X	X	X	X	X	X	X	X		X

TABLE 5. COMPARISON OF PILOT AND FULL-SCALE PLANT EFFLUENT - AVERAGE INSTANTANEOUS VALUES

Parameter	Raw Water	Pilot Plant Effluent	Full-Scale Plant Effluent
Inst THM (ug/L)	1.9	33.6	36.9
TOC (mg/L)	2.9	2.1	1.8
Carbon tetrachloride (ug/L)	<0.1	<0.1	32.
1,2-dichloroethane (ug/L)	<0.1	<0.1	<0.1
Tetrachloroethylene (ug/L)	<0.1	<0.1	<0.1
Arsenic (ug/L)	2.6	<0.1	<0.1
Barium (mg/L)	0.14	0.10	0.12
Cadmium (mg/L)	<0.002	<0.002	<0.002
Chromium (mg/L)	0.014	<0.002	<0.002
Lead (mg/L)	<0.01	<0.01	<0.01
Mercury (ug/L)	<0.2	<0.2	<0.2
Selenium (ug/L)	<1.0	<1.0	<1.0
Silver (mg/L)	<0.001	<0.001	<0.001
Turbidity (NTU)	77.	0.33	0.18
Chlorine (mg/L)	ND	1.5	1.9
Median pH	7.5	7.5	7.4
Temperature (°C)	13.3	---	14.6
Iron (mg/L)	1.3	0.02	0.02
Manganese (mg/L)	0.7	<0.1	<0.1
Coliforms (#/100 mL)	13,050	ND	ND
Total plate count (#/mL)	1,430	2	ND

The only discrepancy between the pilot plant and full-scale plant effluents was the concentration of carbon tetrachloride. The high concentration of carbon tetrachloride in the full-scale plant effluent was suspected of coming from contaminated chlorine gas. This supposition evolved because no carbon tetrachloride was detected in the raw water or in the pilot plant that was being chlorinated using calcium hypochlorite. After the water utility determined the source of the contamination and made the supplier aware of the problem, no further contaminated chlorine gas was received.

Run #2 (Pre and Post Chlorination)

For this run and subsequent runs, the GAC contactors were placed in operation to determine the effectiveness of GAC for the removal of organic compounds present in the raw water as well as those formed in the disinfection process. The number of samples taken in the pilot plant was increased to include the point after mixed media filtration (GAC influent), three locations on the GAC contactor (6, 18, and 30 inches), and at the GAC effluent (78 inches of carbon and 7.7 minutes EBCT). The method of disinfection utilized in the pilot plant for this run consisted of chlorine addition to the raw water and to the GAC effluent just prior to entering the clearwell. The duration of this run was a three week period extending from May 31, 1978 to June 21, 1978.

The instantaneous average data for the plant showed an increase in the total trihalomethane concentration from 1.3 ug/L in the raw water to 31.3 ug/L in the GAC influent. This increase occurred within an elapsed time of 37 minutes. After passing through the carbon contactors, the total instantaneous trihalomethane concentration decreased to 0.1 ug/L. The effect of rechlorination of the GAC effluent is not known because sampling of the clearwell was inadvertently excluded.

Examination of the pilot plant TOC data revealed that the average TOC concentrations decreased through the treatment scheme from 2.6 mg/L in the raw water to 2.1 mg/L after mixed media filtration (GAC influent). The TOC concentration was further reduced to 0.3 mg/L after passing through the GAC contactors.

Bacteriological analyses for this run consisted of total coliforms and standard plate counts. Total coliform counts averaged 4,800/100 mL in the raw water and were not detected after raw water disinfection. Very little regrowth occurred through the carbon with the average GAC effluent containing 1/100 mL. Standard Plate Counts averaged 1,700/mL in the raw water and were attenuated to 1/mL by raw water disinfection. A considerable amount of regrowth was observed in the GAC effluent with the average value increasing to 1,400/mL. Average values for instantaneous samples collected during this run are shown in Table 6.

Table 7 summarizes the averages of the data collected from the three-day stored samples for the pilot plant. The total terminal trihalomethane concentration (TTHM) averaged 144 ug/L in the raw water and was reduced to an average of 6.9 ug/L in the GAC effluent. The concentration of tetrachloroethylene

in the raw water stored samples appears to have increased whereas the average concentrations of the GAC influent and effluent remained the same. Since this same phenomenon was more noticeable in subsequent runs, it will be addressed later.

TABLE 6. AVERAGE PERFORMANCE OF PILOT PLANT (5/31-6/21/78) - RUN #2 (PRE AND POST Cl_2)

Parameter	INSTANTANEOUS Raw Water	GAC Influent	30" GAC	GAC Effluent
Inst THM, ug/L	1.3	31.3	3.4	0.1
TOC, mg/L	2.6	2.1	0.7	0.3
Tetrachloroethylene, ug/L	0.1	0.1	0.1	0.1
Median pH	7.6	8.0	-	7.4
Temperature ^{o}C	23.3	23.6	-	23.4
Turbidity, NTU	72	0.3	-	0.27
Chlorine, mg/L	ND	2.1	-	0.4
Total Coliforms #/100 mL	4800	ND	-	1
Std. Plate Count, #/mL	1700	1	-	1400

TABLE 7. AVERAGE PERFORMANCE OF PILOT PLANT (5/31 - 6/21/78) - RUN #2 (PRE AND POST Cl_2)

Parameter	After 3 DAYS STORAGE Raw Water	GAC Influent	30" GAC	GAC Effluent
Total THM, ug/L	144.	98.	20.6	6.9
Tetrachloroethylene, ug/L	0.5	0.1	<0.1	<0.1
Median pH	8.0	7.9	8.0	7.9
Temperature, ^{o}C	24.	24.1	23.9	23.8
Chlorine, mg/L	1.7	1.9	1.3	1.3

A significant increase in the concentration of instantaneous total trihalomethanes from the raw water to the two plant effluents was caused by raw water chlorination with some slight difference between the two plants attributed to the longer detention time of the full-scale plant. The instantaneous total trihalomethane (Inst THM) concentration was effectively removed by the GAC with no concentration detected at the end of the three week run at the GAC effluent (78 inches of carbon depth). The degree of removal at lesser bed depths varied according to the depth. Equilibrium was reached after one week at the six inch level with no Inst THM concentration detected during the duration of the period at 18 or 30 inches.

Mass spec scans of both the volatiles and extractables were performed on samples collected weekly at various locations in both plants. The analyses were performed to determine if any organic compounds were formed after chlorination of the raw water and if these compounds were subsequently removed by the GAC treatment. Evaluation of this data revealed that the only organics formed were Inst THM and as previously stated, the concentrations of these compounds were effectively reduced by the GAC.

Ten heavy metals were analyzed to determine if any increase in concentration was noticed after GAC treatment when compared to the raw water. Table 8 shows that in only three cases did this occur. One was with selenium (<3.0 to 5.6 ug/L), another one was mercury (<0.3 to 1.0 ug/L), and the third one was a nitrate (0.65 to 0.81 mg/L). These were only scattered instances and cannot be construed as typical occurrences.

As mentioned previously, quality control samples were used as a system and methodology check. In addiition, the low molecular weight volatile organic compounds identified by GC were also verified by GC/MS. Table 9 shows that, in general, the volatiles reported by GC determinations were valid as indicated by GC/MS.

Run #3 (Post ClO_2)

The pilot plant evaluation for run #3 lasted three weeks from August 14, 1978 to September 5, 1978. The treatment method utilized during this mode involved no pre GAC disinfection. Chlorine dioxide disinfection was used only after the GAC contactors. This method of treatment permitted the study of organic removal with GAC without interference from those organic compounds attributed to disinfection. This method was also used to determine if any by-products are formed when chlorine dioxide is used after GAC treatment.

By comparing the average performance values in Table 10, several generalized observations can be made. Since no disinfection was used before the GAC contactors, any removal or reduction in contaminant concentrations can be attributed entirely to the coagulation/settling and filtration steps in the treatment process.

The following were noted after reviewing the average performance values for the pilot plant effluent prior to GAC treatment:

- the instantaneous trihalomethane concentration that existed in the raw water was not significantly reduced during treatment.

TABLE 8. HEAVY METAL CONCENTRATIONS DETECTED IN RUN 2 (PRE AND POST Cl_2)

Parameter		Raw Water			Pilot Plant GAC Effluent			Full-Scale Effluent		
		5/31/78	6/7/78	6/14/78	5/31/78	6/7/78	6/14/78	5/31/78	6/7/78	6/14/78
Arsenic	ug/L	3.4	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Barium	mg/L	0.16	0.09	0.02	0.11	0.07	0.02	0.07	0.08	0.51
Cadmium	mg/L	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001
Chromium	mg/L	0.032	0.009	0.006	0.010	0.004	0.001	0.007	0.004	0.002
Lead	mg/L	0.015	0.010	0.01	<0.008	<0.010	0.01	<0.008	<0.010	<0.010
Mercury	ug/L	0.5	<0.3	<0.3	0.4	<0.3	1.0	0.5	0.6	0.8
Selenium	ug/L	<3.0	<2.0	<2.0	5.6	<2.0	<2.0	<3.0	<2.0	<2.0
Silver	mg/L	<0.002	<0.001	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	0.002
Iron	mg/L	3.2	0.99	1.4	0.02	ND	0.05	ND	0.02	ND
Manganese	mg/L	1.95	0.77	1.23	ND	ND	ND	ND	ND	ND

TABLE 9. VERIFICATION OF VOLATILE ORGANICS BY GC/MS

	$CHCl_3$ ug/L	$CHBrCl_2$ ug/L	$CHBr_2Cl$ ug/L	$CHBr_3$ ug/L	1,2-DCEthane ug/L	CCL_4 ug/L	C_2Cl_4 ug/L
5/31/78							
Raw Water	0.8	0.1	<0.1	<0.2	<0.1	0.1	0.1
	D	D	ND	ND	ND	ND	ND
GAC Inf.	41.	8.6	1.8	<0.2	<0.1	0.1	0.1
	D	D	D	ND	ND	D	D
GAC Eff.	0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
	D	ND	ND	ND	ND	ND	ND
Full Scale Eff.	47.	12.	2.1	<0.2	<0.1	2.1	0.1
	D	D	D	ND	ND	D	D
6/7/78							
Raw Water	0.2	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
	D	D	ND	ND	ND	D	D
GAC Inf.	25.	8.2	1.5	<0.2	<0.1	<0.1	0.1
	D	D	D	ND	ND	D	ND
GAC Eff.	<0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
	D	ND	ND	ND	ND	ND	ND
Full Scale Eff.	36.	12.	2.7	<0.2	<0.1	0.2	0.1
	D	D	D	ND	ND	D	D
6/14/78							
Raw Water	0.7	0.1	<0.1	<0.2	<0.1	<0.1	0.1
	D	D	ND	ND	ND	ND	D
GAC Inf.	22.	7.7	2.1	0.3	<0.1	<0.1	0.1
	D	ND	D	ND	ND	ND	ND
GAC Eff.	0.1	<0.1	<0.1	<0.2	<0.1	<0.1	<0.1
	D	ND	ND	ND	ND	ND	ND
Full Scale Eff.	35.	14.	3.3	<0.2	<0.1	0.1	0.1
	D	D	ND	ND	ND	D	D

TABLE 10. AVERAGE PERFORMANCE OF PILOT PLANT (8/14 - 9/5/78) - RUN #3 (POST ClO_2)

	INSTANTANEOUS			
Parameter	Raw Water	GAC Influent (P.P. Effluent)	30" GAC	Clearwell Effluent
Inst THM, ug/L	1.2	1.1	0.6	0.2
TOC, mg/L	4.2	2.5	1.3	0.8
Tetrachloroethylene, ug/L	0.3	0.2	<0.1	<0.1
Median pH	7.9	7.9	-	7.2
Temperature, ^{o}C	26.8	26.9	-	27
Turbidity, NTU	20.6	0.32	-	0.49
Chlorine, mg/L	ND	-	-	-
Chlorine Dioxide, mg/L	-	ND	-	1.0
Total Coliforms, #/100 mL	5400	3800	-	ND
Std. Plate Count, #/mL	290	45	-	5

- the raw water TOC concentration was reduced by 40 percent from 4.2 mg/L to 2.5 mg/L in the pilot plant effluent (GAC influent).

- the tetrachloroethylene concentration of 0.3 ug/L in the raw water was reduced to 0.2 ug/L.

- a 98 percent reduction in turbidity was achieved from a raw water level of 20.6 NTU to the plant effluent level of 0.32 NTU.

- bacteriological examination shows that both total coliforms and standard plate counts were reduced. Total coliforms went from 5,400 to 3,800 per 100 milliliters and the standard plate count went from 290 to 45 per milliliter.

During this run the average performance values for the pilot plant clearwell were essentially the same as the GAC effluent. The only difference existed in the bacteriological samples. The post GAC chlorine dioxide

disinfection attenuated the coliform count to non-detection while five standard plate counts per milliliter still remained.

Various samples were stored for three days with chlorine and chlorine dioxide. The average concentrations presented in Table 11 show a large increase in the raw water Term THM level when stored with chlorine (1.2 to 247 ug/L, see also Table 10). Because of unreacted chlorine present after generation, a slight increase also occurred with those samples stored with chlorine dioxide (1.2 to 2.9 ug/L) Pilot plant effluent samples showed a Term THM reduction of 43 percent as compared to those from the raw water. Subsequently, the chlorine dioxide stored pilot plant effluent was 52 percent lower than the stored raw water sample.

TABLE 11. AVERAGE PERFORMANCE OF PILOT PLANT (8/14 - 9/5/78) - RUN #3 (POST ClO_2)

	After 3-Day Storage			
Parameter	Raw Water	GAC Influent (P.P. Effluent)	30" GAC	Clearwell Effluent
		Cl_2/ClO_2		ClO_2 only
Total THM, ug/L	247/2.9	141/1.4	56/0.5	0.7
Tetrachloroethylene, ug/L	0.9/0.3	0.6/0.2	0.3/<0.1	<0.1
Median pH	8.0/7.7	7.9/7.8	7.9/7.9	7.8
Temperature, ^{o}C	27/27	27/27	27/27	27
Chlorine, mg/L	1.7	2.5	4.5	-
Chlorine Dioxide, mg/L	1.2	1.9	2.1	2.6

Although not shown in Table 11, the Term THM concentration after 78 inches of carbon was 38 ug/L and 0.7 ug/L respectively for chlorine and chlorine dioxide storage. This constituted an 85 percent reduction in the raw water THMs formed with chlorine storage and a 76 percent reduction with chlorine dioxide storage. These comparisons of precursor removal and subsequent THM reduction were only possible because no predisinfectant was used in the pilot plant during this run.

Because of the ability to compare the effects of sample storage with chlorine and chlorine dioxide, a phenomenon was notice when tetrachloroethylene was evaluated. Table 11 shows that the average value of tetrachloroethylene increased upon storage with chlorine whereas with chlorine dioxide the stored sample values were identical to the instantaneous values presented in Table 10. This phenomenon was not produced by averaging individual data, but actually occurred on practically every sampling day as shown in Table 12.

As previously mentioned, TOC concentrations were reduced after pilot plant treatment by about 40 percent. Complete treatment, including GAC, reduced TOC concentrations by 80 percent with only a slight increase in effluent levels noted at the end of the three week operation.

At GAC depths of 6 and 18 inches, breakthrough occurred in TOC concentrations in about one week. At 30 and 78 inches, no breakthrough was detected during the duration of the run.

The qualitative mass spec scan data for this run did not indicate that any organic by-products were formed after chlorine dioxide disinfection for the compounds evaluated. As in run #2, however, there was not an abundance of data available for comparison. The long-term runs presented later provided more data for creditable evaluation.

A slight increase in some heavy metal concentrations was noted in the GAC effluent as compared to the raw water. This increase was recorded twice with barium (0.12 to 0.15 mg/L and 0.02 to 0.05 mg/L) and in one instance with lead (<0.01 to 0.03 mg/L)

Run #4 (Pre and Post ClO_2)

The objectives of run #4 were to determine if any by-products were formed when chlorine dioxide was used as a pre-disinfectant, and to evaluate GAC removal of any organic compounds present or formed in the water. This run started on November 13, 1978 and continued for three weeks to December 6, 1978. The mode of operation utilized for this run consisted of chlorine dioxide addition to both the raw water and the GAC effluent.

As anticipated, very little increase in the Term THM was observed while disinfecting with chlorine dioxide. Any increase that did occur can probably be attributed to a small amount of unreacted chlorine in the ClO_2. Average concentrations for the Inst THM are presented in Table 13 which shows the raw water value of 3.6 ug/L being reduced to 0.2 ug/L in the pilot plant clearwell. Very similar values were noted for the Term THM (3.7 ug/L for the raw water and 1.1 ug/L for the clearwell when stored with ClO_2.

By comparing the GAC influent with the comparable full-scale plant effluent for TOC, Figure 3 shows that the use of the full-scale plant for a control was still valid. It can also be seen from this figure that although the raw water TOC concentration increased, the GAC effectively kept the level constant within the three-week period. Six inches of carbon was effective for only two days whereas 18, 30, and 78 inches of carbon effectively removed the TOC for the duration of the run.

TABLE 12. TETRACHLOROETHYLENE CONCENTRATIONS UPON STORAGE WITH CHLORINE AND CHLORINE DIOXIDE

	Raw Water			GAC Influent (P.P. Effluent)			GAC Effluent			Clearwell Effluent			Full Scale Effluent		
Date	Inst.	Stored		Inst.	Stored		Inst.	Stored		Inst.	Stored		Inst.	Stored	
		Cl_2	ClO_2		Cl_2	ClO_2		Cl_2	ClO_2		Cl_2	ClO_2		Cl_2	ClO_2
8/14/78	0.4	0.4	0.1	0.2	0.5	0.1	0.1	<0.1	<0.1	<0.1	-	<0.1	0.3	0.8	-
8/16/78	0.6	1.0	0.5	0.5	0.6	0.5	<0.1	<0.1	<0.1	<0.1	-	<0.1	0.8	0.8	-
8/18/78	0.7	1.3	1.0	0.5	0.9	0.4	<0.1	<0.1	<0.1	<0.1	-	<0.1	0.9	0.7	-
8/21/78	0.1	0.5	0.3	0.2	0.5	0.1	<0.1	<0.1	<0.1	<0.1	-	<0.1	0.3	0.5	-
8/23/78	0.2	0.6	0.2	0.1	0.6	0.1	<0.1	<0.1	<0.1	<0.1	-	<0.1	0.8	0.3	-
8/25/78	0.1	0.4	0.1	0.1	0.2	0.1	0.1	0.4	0.1	0.2	-	<0.1	0.3	0.4	-
8/28/78	0.2	2.5	0.1	0.1	0.5	<0.1	<0.1	0.6	<0.1	<0.1	-	<0.1	0.7	0.7	-
8/30/78	<0.1	0.4	<0.1	0.1	0.9	<0.1	<0.1	0.1	<0.1	<0.1	-	<0.1	1.2	0.4	-
9/5/78	0.8	0.8	0.1	0.1	0.5	0.1	<0.1	<0.1	<0.1	<0.1	-	<0.1	0.4	0.9	-

NOTE: All concentrations are in ug/L

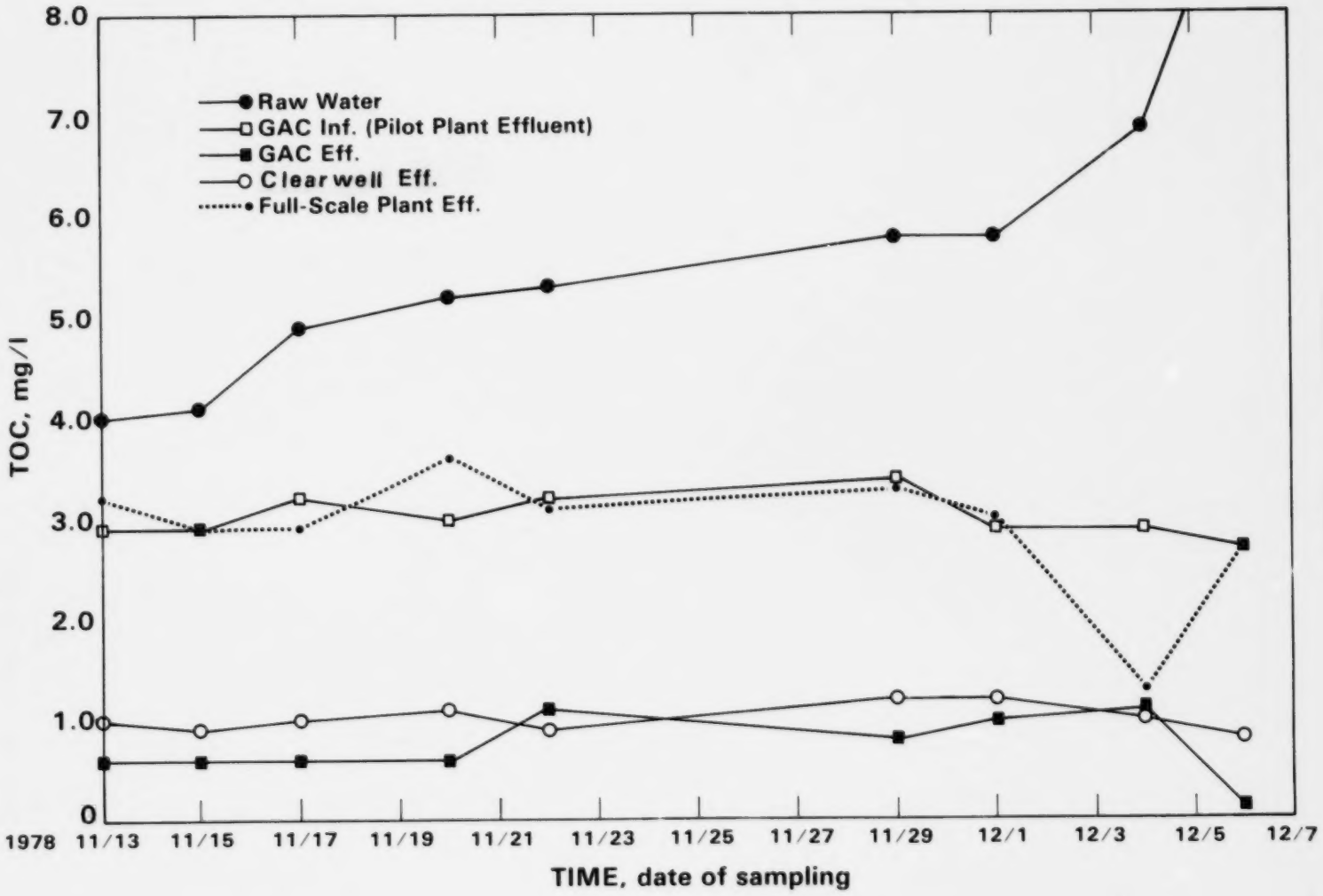

FIGURE 3. COMPARISON OF TOC CONCENTRATION THROUGH PILOT AND FULL-SCALE PLANT.

Samples stored with chlorine dioxide did not increase in tetrachloroethylene concentration when compared to their corresponding instantaneous samples. Only the raw water and full-scale plant effluent samples were stored with chlorine and each showed varying degrees of increases in the tetrachloroethylene concentration. These results compare closely to that observed in run #3.

TABLE 13. AVERAGE PERFORMANCE OF PILOT PLANT (11/13 - 12/6/78) - RUN #4 (PRE AND POST ClO_2)

Parameter	Instantaneous			
	Raw Water	GAC Influent (P.P. Effluent)	30" GAC	Clearwell Effluent
Inst THM, ug/L	3.6	2.5	0.7	0.2
TOC, mg/L	5.7	3.0	1.6	1.0
Tetrachloroethylene, ug/L	0.4	0.4	<0.1	<0.1
Median pH	7.6	7.6	-	7.3
Temperature, °C	12.7	13.3	-	13.2
Turbidity, NTU	95.	0.7	-	0.5
Chlorine Dioxide, mg/L	ND	0.1	-	1.0
Total Coliforms #/100 mL	6300	ND	-	ND
Std. Plate Count #/mL	6200	16	-	4

The data displayed in Table 14 show that a raw water chlorine dioxide dosage of approximately 4 mg/L was quickly depleted in the pilot plant to 0.3 mg/L or less (GAC influent). Although the total coliforms were eliminated, the standard plate count was not reduced to an acceptable level in the GAC influent. These counts proliferated in the GAC contactor and were not completely eliminated by the one mg/L chlorine dioxide dosage applied to the GAC effluent. The total coliform bacteria did not show regrowth in the GAC contactor and were never detected in the clearwell effluent. Only one incident of a standard plate count occurred in the full-scale plant and it was one per milliliter.

TABLE 14. BACTERIOLOGICAL QUALITY OF VARIOUS SAMPLING POINTS IN RUN 4.

	Raw Water			GAC Influent			GAC Effluent			Pilot Plant Eff.			Full Scale Eff.		
Date	Coli. #/100 mL	SPC #/ml	Res. ClO_2 mg/L	Coli. #/100 mL	SPC #/mL	Res ClO_2 mg/L	Coli. #/100 mL	SPC #/mL	Res ClO_2 mg/L	Coli. #/100 mL	SPC #/mL	Res ClO_2 mg/L	Coli. #/100 mL	SPC #/mL	Res ClO_2 mg/L
11/13/78	1,100	1,200	-	0	3	0.15	0	480	0	0	1	1.8	0	0	2.8
11/15/78	1,300	390	-	0	6	0.2	0	1,540	0	0	3	0.8	0	0	2.2
11/17/78	14,000	9,200	-	0	3	0.2	0	2,140	0	0	1	1.0	0	0	2.1
11/20/78	2,800	5,700	-	0	7	0.3	0	760	0.1	0	6	1.0	0	0	3.0
11/22/78	2,600	6,700	-	0	3	0.23	0	1,040	0	0	3	0.8	0	0	3.0
11/29/78	4,300	9,100	-	0	13	0	0	1,570	0	0	6	0.8	0	0	2.0
12/1/78	5,900	10,100	-	0	49	0.2	0	3,340	0	0	6	0.8	0	0	2.3
12/4/78	5,900	7,100	-	0	31	0	0	40	0	0	2	1.0	0	0	2.6
12/6/78	19,000	6,400	-	1	30	0	0	10,840	0	0	7	0.9	0	1	1.2

	pH Range	Turbidity Range (NTU)
Raw Water	7.4 - 7.9	12. - 440.
GAC Inf.	7.2 - 7.7	0.3 - 1.4
GAC Eff.	7.2 - 7.6	0.22 - 0.68
Pilot Plant Eff.	7.0 - 7.7	0.34 - 0.58
Full Scale Eff.	7.2 - 7.8	0.16 - 0.32

In order to determine what changes occurred with chlorine dioxide, chlorite and any residual chlorine within the pilot plant treatment scheme, a profile was run during two days of operation. The analyses were performed using both the La Motte-Palin Modified titration procedure[2] and the chlorophenol red titration method[22] developed by Olin Corporation.

Table 15 shows the concentrations of chlorine dioxide, free chlorine, and chlorite for various points in the pilot plant. Generally, as the chlorine dioxide concentration decreased, the chlorite concentration increased. Since the increase was not proportional, this indicated that other species such as chloride and chlorate were probably formed. Any chlorite present in the GAC influent was substantially reduced in the carbon contactor.

As in previous runs, the qualitative mass spec scans did not indicate the formation of organic by-products evaluated relative to this mode of treatment. The mass spec scans used for volatile confirmation generally showed that the GAC reported values were valid.

No increase in the concentration of metals occurred after passage through the carbon contactor. Any slight increase noted at other sampling locations when compared to the raw water can probably be attributed to analytical error.

Summary and Findings

After completion of the short-term pilot plant studies a comparison of their performance for the major parameters of interest satisfied the objective of selection of an operational mode for long-term studies. The data was reviewed with the water consumer in mind. For instance, at the time of this study, the THM regulations were being proposed and with normal plant operation using pre- and post-chlorination, the maximum allowable limit would be exceeded during part of the year. Therefore, a mode of operation was needed that would produce less THMs, but retain the required disinfection capability.

Using Table 4 as a reference point, run 3 was eliminated from possible selection because the plant could not operate without a raw water disinfectant (slime growth created a problem). Although GAC was included in the study for removal of any specific organics that might be present, the reduction of THMs by an operational change was preferred. Therefore, Run 4 was selected as the operational mode for further studies because:

- low Inst THM values were produced through mixed media filtration (< 5.0 mg/L)
- THM precursor was reduced thus producing less Term THM than with pre-chlorination.
- total coliforms and standard plate count were effectively controlled.

- no organic by-products peculiar to this run were noted when looking at the priority pollutants.

During the course of these short-term studies, some observations were noted:

- with chlorination, the Inst THM concentration increased during treatment through mixed media filtration.
- with chlorine dioxide disinfection, much lower Inst THM concentations were produced.
- TOC concentrations were reduced around 40 percent by conventional treatment.
- both chlorine and chlorine dioxide disinfection was effective for control of total coliform and standard plate count.
- the raw water turbidity was reduced by greater than 98 percent through mixed media filtration.
- mass spec scans for the priority pollutants showed no organic by-products formed except Inst THMs.
- upon storage with a chlorine residual, tetrachloroethylene concentration incresaed in some instances. No increases were noted with chlorine dioxide.
- in general, no heavy metal concentration increase was noticed after GAC treatment.

TABLE 15. CHLORINE DIOXIDE PROFILE THROUGH PILOT PLANT FOR RUN 4.

Date	Sampling Location	mg/L ClO_2		mg/L Free Cl_2		mg/L Chlorite	
		LaMotte	CPR	LaMotte	CPR	LaMotte	CPR
12/1/78	Out of Generator	304.	300.	ND		128.	
	Raw Water Dosage	3.8	3.8	ND		1.6	
	Rapid Mix Chamber	0.9	-	ND		1.5	
	After Settling	0.6	0.8	ND		1.8	
	GAC Influent	0.2	0.2	ND		2.1	
	GAC 6"	ND	ND	ND		2.4	
	GAC 18"	ND	ND	ND		1.8	
	GAC 30"	ND	ND	ND		1.5	
	GAC Eff. (78")	ND	ND	ND		0.4	
	Clearwell	0.9	0.8	0.2		0.6	
12/5/78	Out of Generator	333.	300.	15.		150.	
	Raw Water Dosage	4.2	3.8	0.2		1.9	
	After Settling	0.5	0.2	0.1		2.3	
	GAC Influent	ND	ND	0.1		3.0	
	GAC 6"	ND	ND	ND		2.6	
	GAC 18"	ND	ND	ND		2.1	
	GAC 30"	ND	ND	ND		1.6	
	GAC Eff. (78")	ND	ND	ND		0.3	
	Clearwell	1.1	0.8	0.3		0.9	

SECTION 7

LONG-TERM PILOT PLANT OPERATION

As shown in Section 6, three different experimental modes of operation for the pilot plant were evaluated for selection of the "best" operational mode for long-term studies. The selected mode consisted of pre- and post-chlorine dioxide disinfection. Using this selected mode, four runs were completed that consisted of continuous pilot plant operation for approximately three months each. The length of these runs was determined by evaluating the TOC and Inst THM for GAC exhaustion. These were the only consistent parameters that could be used. For all runs, the performance of the pilot plant through GAC treatment was compared with the performance of the full-scale plant under normal operation (pre- and postchlorine disinfection). Because the long-term performance of the pilot plant closely simulated the short-term performance, GAC use will be discussed first.

GAC Handling and Reactivation

ICI's Hydrodarco 10x30 lignite-base GAC was used in the study. Each contactor, when filled to approximately 78 inches contained between 545 and 590 kilograms (1,200 and 1,300 lbs.) of GAC. The GAC was introduced into the contactors, and backwashed for about 2.5 hours at 303 liters/min. (80 gpm) to remove the fines.

When the GAC was to be reactivated it was educted into epoxy-coated 208-liter (55 gallon) drums containing well screens. The well screens allowed for dewatering of the GAC after eduction and reactivation. On all but one run, the GAC in the drums was shipped to Passaic Valley, New Jersey for reactivation.

A 45.4-kg (100-lb) per hour Shirco infrared furnace was used for reactivation of the spent GAC. The GAC was unloaded directly from the 208-liter (55-gallon) drums into a small hopper at the base of the carbon-feed screw conveyor. This GAC was dewatered by the conveyor to approximately 50 percent moisture and fed into the furnace where it dropped onto a woven wire conveyor belt and was leveled into a layer approximately 1.9 cm (3/4 inch) thick. The conveyor belt moved the GAC underneath infrared heating elements that provided the energy necessary to dry the carbon, drive off adsorbed compounds, and restore the pore structure.

Process temperatures were controlled in zones and typically ranged from 1200°F in the drying zone to about 1650°F in the reactivation zone. The furnace exhaust temperature was about 1200°F and the wet-scrubbed exhaust gases discharged to the atmosphere ran about 100°F. Residence time of the GAC in the furnace was from twenty to thirty minutes. Reactivated GAC was quenched and transported back to the drums for shipment to Evansville.[1]

During each of three reactivations, furnace operational results were maintained by the furnace vendor. The reported results were as follows:[3,4,5]

TABLE 16. OPERATIONAL DATA FOR INFRARED FURNACE

Furnace Operational Data	Reactivation Run 1	2	3
Length of GAC reactivation run, hrs.	27	18	30
GAC feed rate, lbs/hr	80	75	69
Avg. GAC moisture after feed screw, %	52.9	50	50
Total energy consumption, KWH	1,750	1,040	1,062
Specific energy consumption, KWH/lb of GAC reactivated	0.79	0.80	0.97

The infrared furnace used in this study did not have an afterburner for incinerating any residual organic compounds that may have been present in the furnace off-gases. Stack testing was not done for this study because of the limited knowledge for sampling and analyses of low concentrations of organics and the availability of a suitable analytical laboratory to carry out the proper testing.

By evaluating the specific organics in the GAC influent, there seemed to be none of significant concentration. However, the total organic halides (TOX) of this same water indicated that there was between 56 - 69 ug/L of TOX. Also, samples of the furnace scrubber effluent for pH showed that it was typically 3.6 as compared to 7.5 - 7.9 for the scrubber supply water.[3] This acidic value is suspected of being indicative of decomposition/combustion of chlorinated organic compounds within the furnace followed by the production of hydrochloric acid during the wet scrubbing process. Therefore, it is possible that a small amount of organics was discharged to the atmosphere.

GAC Losses

An estimate of the GAC losses from reactivation was determined by the furnace vendor. The level of GAC in each 208-liter (55-gallon) drum received at Passaic Valley from Evansville was measured. After reactivation, the drums were refilled to the same level with GAC and allowed to drain through the well screens. The reduction in GAC level in the last drum was used to estimate volumetric losses attributable to reactivation. By using this method, an overall reactivation loss of about 5 percent was reported.[3,4,5]

Volumetric measurements for determining total system losses (handling, transport, and reactivation) were also done at Evansville. The height of the GAC in the contactor was measured after being backwashed and drained before the contactor was placed in operation. After the reactivated GAC was placed in the same contactor and backwashed and drained, height measurements were again collected. The difference between these two measurements was used to estimate the total system losses.

Although the surface of the GAC in the contactor was essentially level, no surface profile was determined by multiple measurements. Therefore, the losses reported can only be considered as estimates. These total system losses ranged from 6.5 to 9.0 percent with an average loss of about 8 percent.

At another location, using a 15.9 kg (35 lb) per hour infrared furnace, total system losses ranged from 11 percent with the first reactivation to 8 percent for the third reactivation.[6] Furnace losses were estimated to be 9 and 6 percent, respectively, for the first and third reactivation leaving about 2 percent losses for handling and transport of the GAC. Possible reasons given for the decrease in losses from the first to third reactivation were:

- improved knowledge and operation of the furnace
- burning off of softer material in first reactivation, so that GAC particle was harder by third reactivation. Only the second possibility applies to Evansville because the vendor operated the infrared furnace.

GAC Properties

Composite samples of spent and reactivated GAC were collected during each run. As the spent GAC was educted from the contactor, periodic samples were taken representing the total volume of GAC. These individual samples were combined to produce a single sample for analyses of GAC properties. In addition, as the reactivated GAC was educted back into the contactor, several individual samples were again taken and combined into one representative sample. The virgin sample was taken directly from the shipping bag.

These samples were sent to Georgia Tech Engineering Experimental Station for analysis. A summary of the data for all the runs is presented in Table 17.

One of the easier properties to determine that is widely accepted as an immediate indication of the efficiency of the reactivation process is the apparent density. By looking at Table 17, the apparent density only increased slightly from 0.427 to 0.440 g/mL. As discussed by McGinnis,[7] this would indicate an optimum reactivated GAC situation because:

- the reactivity of the adsorbate char is greater than that of the original GAC and any attempt to completely remove that char would typically result in damage to the original GAC pore structure.

TABLE 17. SUMMARY OF GAC PROPERTIES

Property	Run 1			Run 2			Run 3	
	V	S	R	V	S	R	S	R
BET Surface Area, m^2/g	597	-	675	516	-	644	-	688
Iodine No., mg/g	617	470	638	439	432	596	467	650
Modified Phenol Value, ppm	30.4	48	31.5	51.9	37.2	28.5	61.8	30.4
Molasses Decolorizing Index, DI Units	18.5	12.5	17.8	10.2	9.8	14.7	10.4	13.7
Moisture, %	-	50.4	58.9	53.9	52.6	57.0	55.4	51.5
Ash, %	15.3	13.8	13.9	14.8	14.8	15.7	16.5	17.9
Volatile Matter, %	7.4	27.7	6.4	11.8	12.4	6.6	11.0	6.1
Apparent Density, g/mL	0.427	0.554	0.447	0.424	0.434	0.403	0.443	0.440
Screen Analysis, %								
0-10	1.3	0	0	0.1	0	0.1	0	0
10-12	6.9	2.6	2.8	2.8	2.8	1.9	1.4	1.0
12-16	52.5	39.6	40.7	45.0	37.1	37.8	31.6	19.2
16-20	33.1	41.4	40.5	38.9	40.3	43.0	44.0	40.4
20-30	6.0	12.6	12.6	10.9	14.3	13.1	18.5	26.4
Through 30	0.2	3.8	3.4	-	-	-	-	-
30-40	-	-	-	1.6	3.2	2.5	3.6	8.6
Through 40	-	-	-	0.6	2.2	1.6	0.9	4.4
Particle Diameter (Calc. mean), mm	1.29	1.13	1.14	1.18	1.11	1.12	1.08	0.937
Abrasion No., % by mean particle diameter	18.5*	14.2*	21.9*	43.6	48.4	50.7	47.7	50.8

*Used 50 g sample, instead of normal 100 g sample.
V = Virgin GAC
S = Spent GAC
R = Reactivated GAC

- some shrinkage occurs during reactivation of the GAC resulting in a slight increase in the apparent density.

When looking at all the runs, a trend appeared to develop for the iodine number and molasses decoloring index with the data showing that the spent GAC was restored to essentially the virgin state. The iodine number increased from 617 to 650 mg/g and the decolorizing index decreased from 18.5 to 13.7. This trend does indicate some pore structure change with the increased iodine number associated with smaller pores and a greater affinity for low molecular weight organics, while the decrease in the decolorizing index means less larger pores were available to adsorb the higher molecular weight organics.

Although the theoretical capacity of the GAC for the trihalomethanes and other specific organics probably increased, and for the trihalomethane precursors, decreased, no indication of this phenomenon was evident in the raw data. During subsequent runs, the ash content increased from 15.3 to 17.9 percent indicating deposition of inorganic materials on the GAC during service, but with no reduction in the GAC adsorptive capacity.

During the subsequent reactivations, there was a decrease in the size of the GAC particles. This was illustrated by the mean particle diameter as shown in Table 17. The average of two virgin samples gave a mean particle diameter of 1.24 mm. The mean particle diameter for the first reactivation dropped to 1.14 mm and by the third subsequent reactivation was 0.937 mm. Particle size measurements determined by screen analyses also showed the same trend (Figure 4). This reduction in the particle size indicates that some attrition to the GAC particle did occur during reactivation with some accumulation of fines.

Cumulative surface area distribution curves shown in Figure 5 indicate that the reactivated GAC for all cycles had a total surface area greater than the virgin GAC. This additional surface area was developed primarily in the small pore region of less than 30 Angstroms, although there was a noticeable difference between the virgin and subsequent reactivated GAC at pore diameters less than 200 Angstroms.

The iodine number and cumulative surface area correlated almost exactly indicating that the pores were opened and maintained so that there was an unlikelihood of any gradual degradation of adsorptive capacity after subsequent reactivations. The ratios that developed for BET Surface Area/Iodine Number for an average of two virgin samples and three subsequent reactivation cycles were 1.08, 1.06, 1.08, and 1.03 respectively. This direct correltion between the iodine number and total surface area agrees with that shown by Juhola.[8]

GAC Contactor Performance Comparison

During this performance evaluation of the identical parallel contactors, GAC exhaustion was determined by TOC and Inst THM. Only these two parameters were evaluated for exhaustion because the other organics were only detected on a sporadic basis.

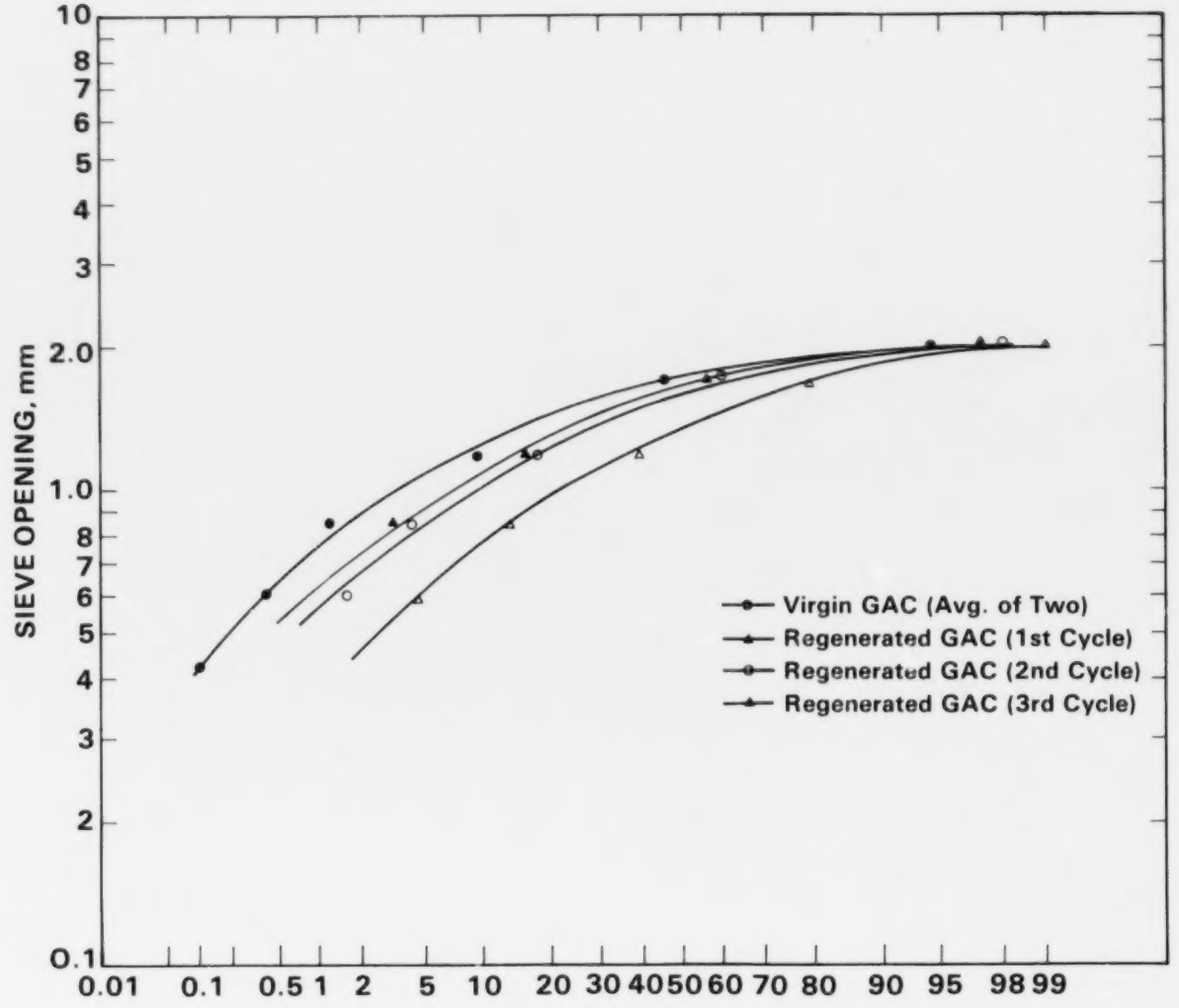

FIGURE 4. PARTICLE SIZE DISTRIBUTIONS - CUMULATIVE PERCENT PASSING.

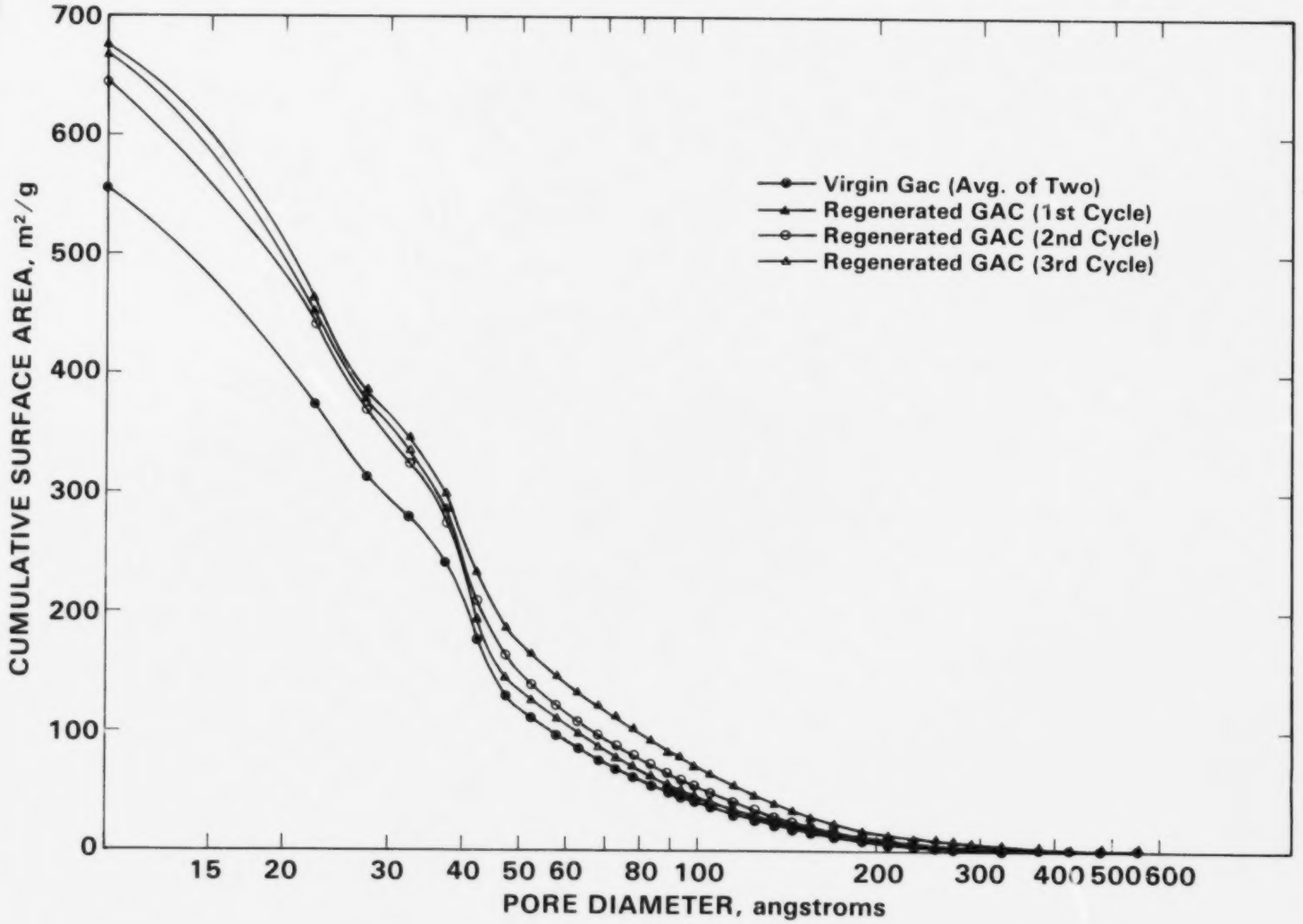

FIGURE 5. CUMULATIVE SURFACE AREA DISTRIBUTIONS BY NITROGEN DESORPTION.

The performance of the two parallel GAC contactors was compared while using identical flows of 153 L/min (40.4 gpm) to each contactor that contained approximately the same amount of virgin GAC (559 and 567 kg-1231 and 1249 lbs) at an EBCT of 9.6 minutes. The two contactors performed similarly. With an influent TOC concentration of 2-3 mg/L, the contactor effluents followed each other closely and rose from about 0.5 mg/L at the beginning of the run to about 1.6 mg/L after 90 days of operation (Figure 6). Correspondingly both contactors removed about 75 percent of the TOC at the start of the run and by day 60 removed only 30 percent, although this removal remained fairly constant even with a fluctuating influent (Figure 7).

In comparing the side-by-side performance of virgin GAC, instantaneous trihalomethanes (InstTHM) were also evaluated. The InstTHM was formed by unreacted chlorine used in the production of chlorine dioxide. Even at the low concentrations (< 5 mg/L) shown in Figure 8 applied to the GAC, equilibrium was reached in about 60 days. This observation should make one careful when assuming that low applied concentrations will allow for extended GAC operation before exhaustion. Other related studies have shown similar observations at low applied InstTHM concentrations.[9]

By observing the GAC performance for InstTHM in Figure 8, breakthrough can be seen in about 40 days with equilibrium occurring around 60 days. Both contactors performed essentially the same, but one would not have expected equilibrium to occur at a concentration much above the applied concentration.[9,10] A completely satisfactory reason for this phenomenon has not been established, but Moore[11] has suggested that possibly hydrolysis of trichloroacetic acid has occurred. Others have suggested possibilities such as chromatographic effect, but this has been ruled out. Regardless of the cause of the apparent formation of THMs, these are low InstTHM concentrations much below the promulgated regulation of 0.1 mg/L.

As shown above, TOC concentrations were at steady-state in about 60 days and InstTHM concentrations reached equilibrium in about the same time period. Although the GAC was exhausted in about 60 days, each run was allowed to continue for approximately 90 days. This extension was needed to collect enough data to be sure that the parameter concentrations had actually reached steady-state or equilibrium conditions.

Performance of Virgin vs. Reactivated GAC for TOC and THM Control

The original spent virgin GAC was reactivated subsequently three times. Except for the first reactivation, make-up virgin GAC was required to replenish losses resulting from handling and reactivation. For each run, fresh virgin GAC was added to one contactor (T_4P) and its performance was compared to the subsequent reactivated GAC in the parallel contactor (T_5P). As shown previously, the GAC properties indicated that reactivation had restored the GAC to its virgin state, or possibly somewhat better than the virgin conditions. Again, the Inst THMs and TOC were used to evaluate the performance of the two GAC contactors. Other parameters that were also analyzed in conjunction with these two performance evaluation parameters will be discussed later in the report.

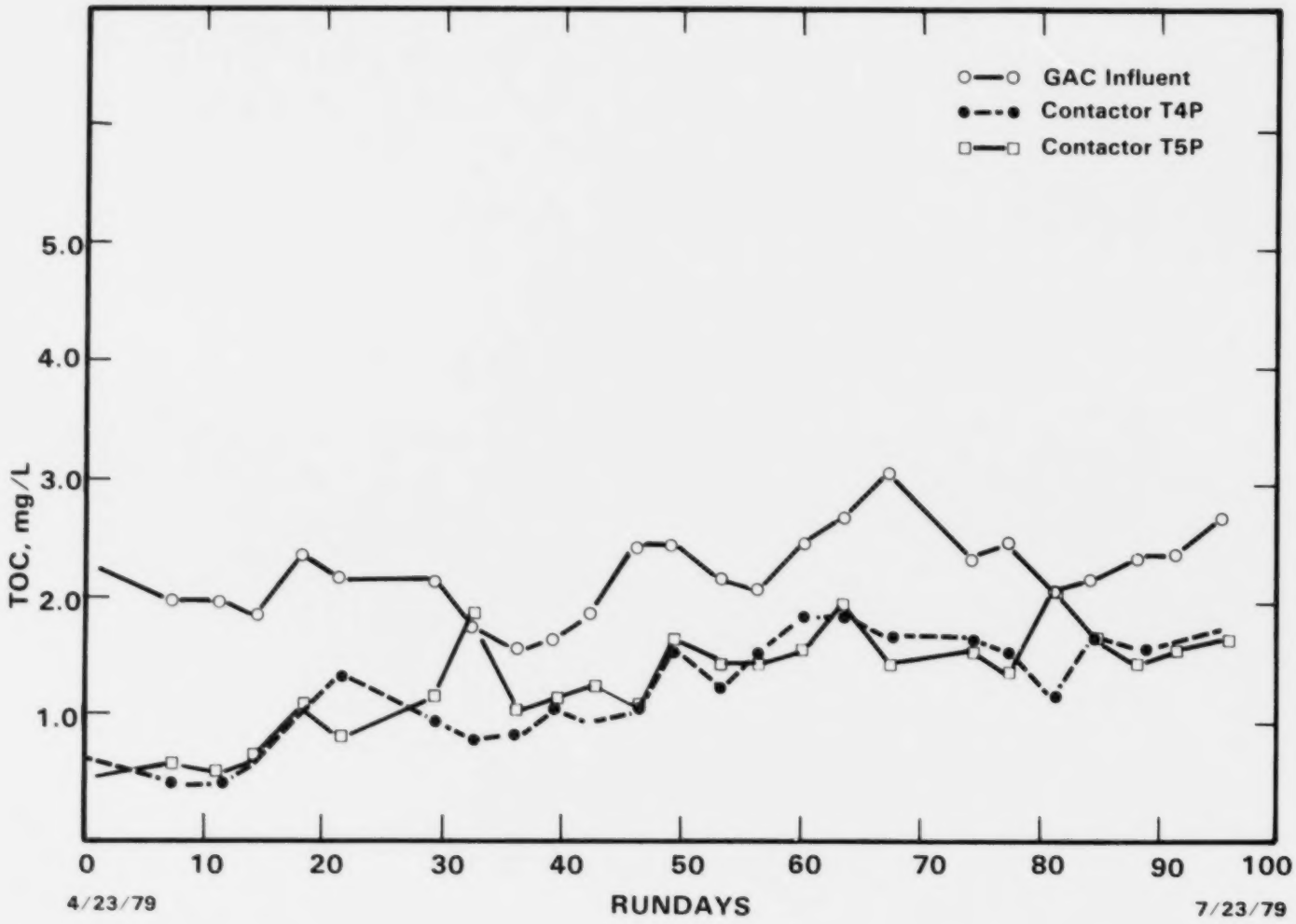

FIGURE 6. TOC REMOVAL BY VIRGIN GAC.

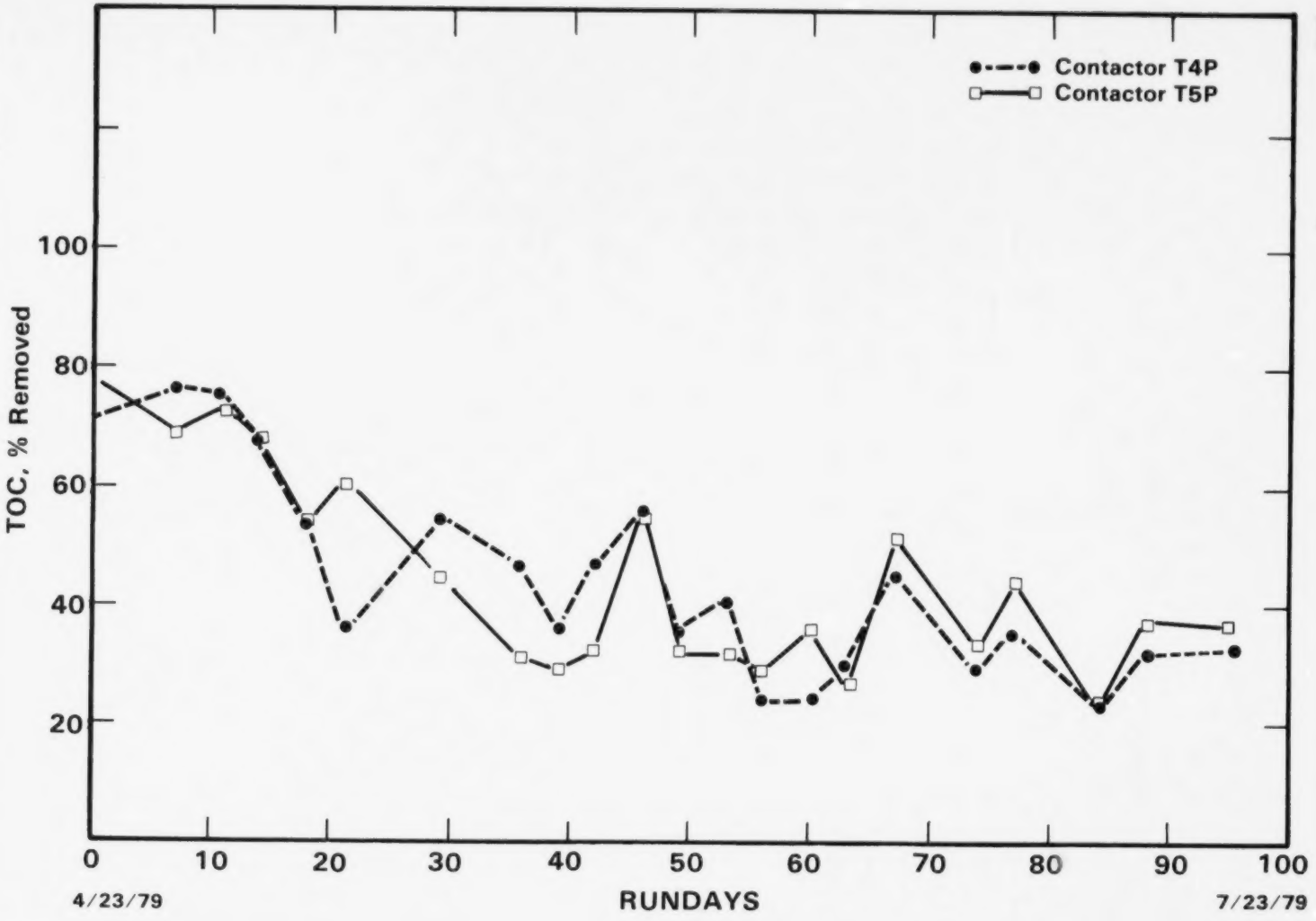

FIGURE 7. PERCENTAGE TOC REMOVAL BY VIRGIN GAC.

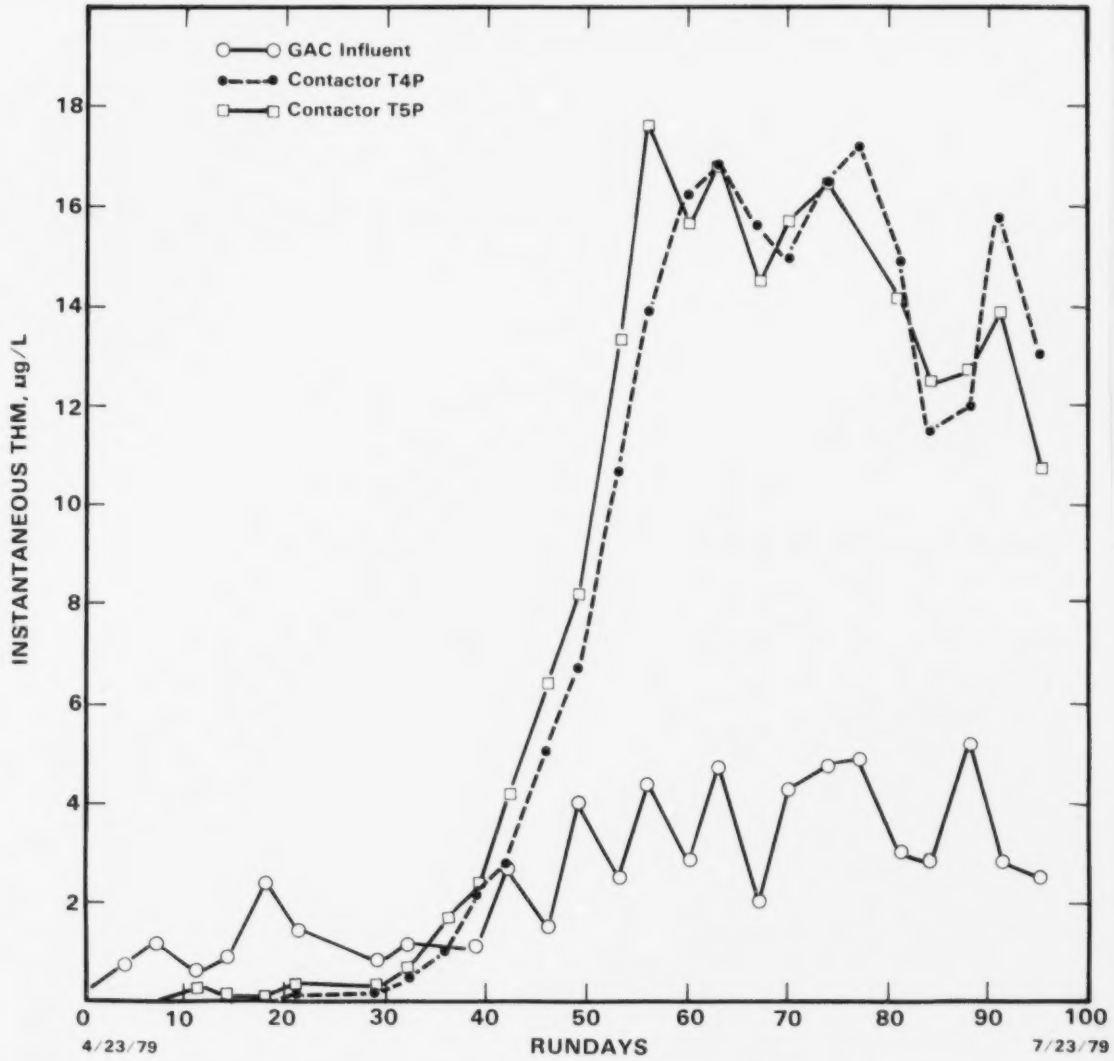

FIGURE 8. INSTANTANEOUS THM PERFORMANCE THROUGH VIRGIN GAC

The amount of GAC placed in each contactor for all runs was as near the same as possible. As shown in the following table, this amount ranged from 580 to 648 kg (1277 to 1427 lbs).

TABLE 18. AMOUNT OF GAC IN CONTACTORS

	Run 6		Run 7		Run 8	
	Vir.	1st React.	Vir.	2nd React.	Vir	3rd React.
Weight kg (lbs)	595 (1310)	648 (1427)	609 (1341)	580 (1277)	610 (1343)	630 (1387)

Vir. = Virgin
React. = Reactivation

Also, the flow through the pilot plant filter was split so that a portion as equal as possible was sent to each parallel contactor for all runs. The actual total flow for each contactor for each run after a common length of time (84 days) is shown in Table 19.

The flow through the reactivated GAC contactor was always somewhat less than that through the virgin contactor. Although the applied flow at the start of each run was essentially the same to both contactors, this difference in the total flow between the contactors is attributed to carbon fines not completely removed from the reactivated GAC and a reduction in particle size, resulting in compaction and flow restriction. At the beginning of each run, several hours of backwashing was used for GAC fine removal as shown in Table 20.

By evaluating the selected GAC performance parameters (TOC and THM) for each of the runs, an indication of the performance of virgin and subsequent reactivated GAC was established. As mentioned previously, the virgin GAC that was used in the first run was subsequently reactivated three times. In comparing the performance of virgin and once reactivated GAC, the effluent TOC concentration of both was practically identical as shown in Figure 9. Again, this was shown in the parallel comparison of virgin and twice reactivated GAC (Figure 10).

In these two runs, the effluent TOC concentration from the GAC contactors followed each other closely indicating similar GAC performance. In the last run, where virgin GAC was compared to thrice reactivated GAC, the effluent TOC concentration from both contactors was somewhat scattered, but the overall average effluent concentration was about the same (Figure 11). Actually, the average TOC effluent concentration for all the runs where virgin GAC was compared to subsequently reactivated GAC was essentially the same as shown in Table 21.

When looking at the applied TOC concentration to the GAC contactors for all runs, Figure 12 shows that this concentration was somewhat but not radically different. These concentrations ranged from 1.6 to 3.0 mg/L with the lowest concentrations seen during the months of March-May. The effluent

TABLE 19. TOTAL FLOW THROUGH GAC CONTACTORS AFTER 84 DAYS OF OPERATION

	Run 6		Run 7		Run 8	
	Vir.	1st React.	Vir.	2nd React.	Vir.	3rd React.
Flow m^3 ($galx10^3$)	15,299 (4042)	13,690 (3617)	16,101 (4254)	15,193 (4014)	19,796 (5,230)	16,007 (4,229)

Vir. = Virgin
React. = Reactivated

TABLE 20. GAC BACKWASH RATE BEFORE START OF EACH RUN

Vir. vs. 1st React.	Vir. vs. 2nd React.	Vir. vs. 3rd React.
3 hrs @ 0.3 m^3/min (80 gpm)	4 hrs @ 0.3 m^3/min (80 gpm) 9 hrs @ 0.15 m^3/min (40 gpm) 0.5 hrs @ 0.3 m^3/min (80 gpm)	4.5 hrs @ 0.3 m^3/min (80 gpm) 4.5 hrs @ 0.15 m^3/min (40 gpm) 5.5 hrs @ 0.15 m^3/min (40 gpm)
Total Flow = 54.5 m^3 (14,400 gal)	163.5 m^3 (43,200 gal)	172.6 m^3 (45,600 gal)

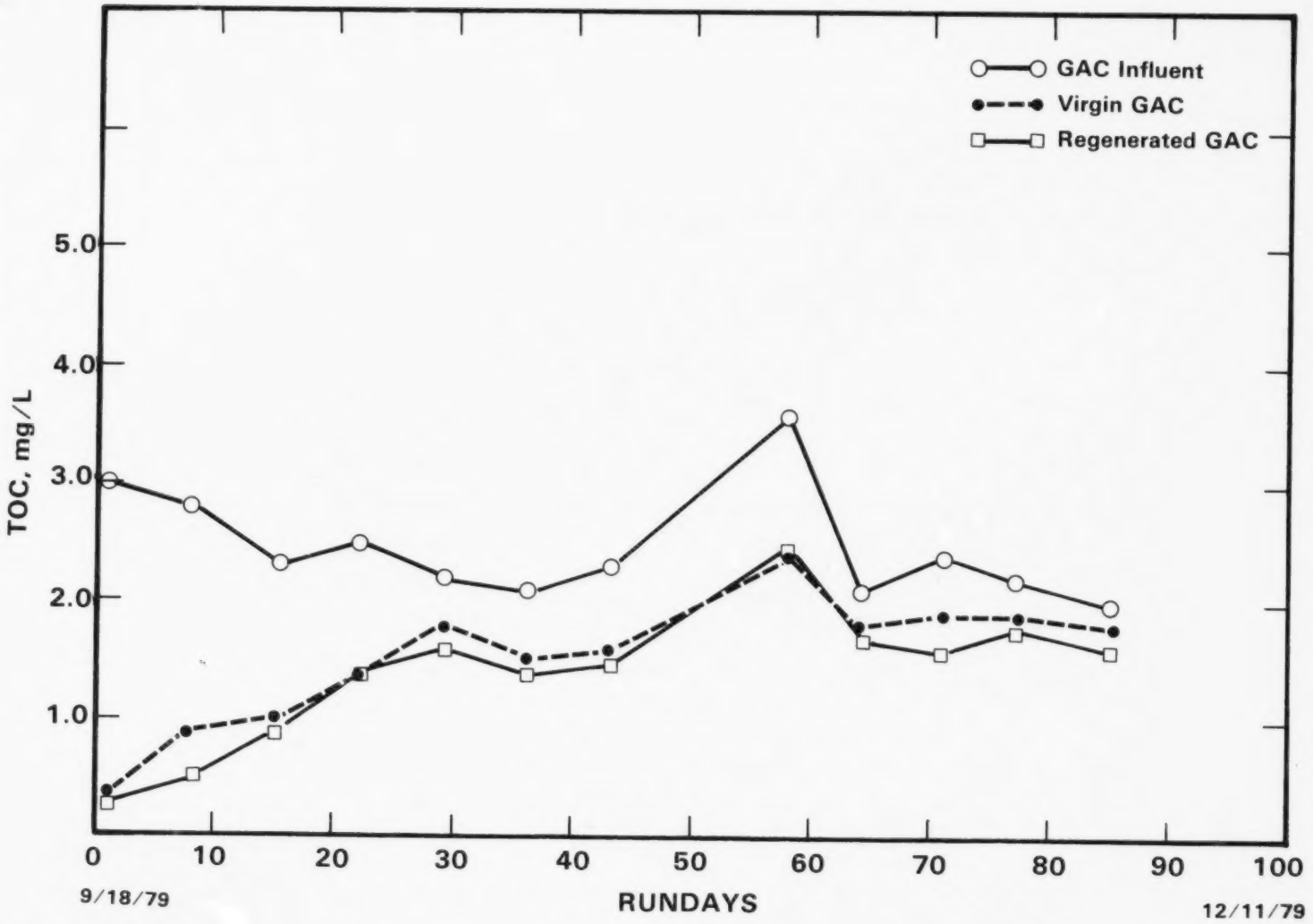

FIGURE 9. COMPARISON OF VIRGIN AND ONCE REACTIVATED GAC - TOC.

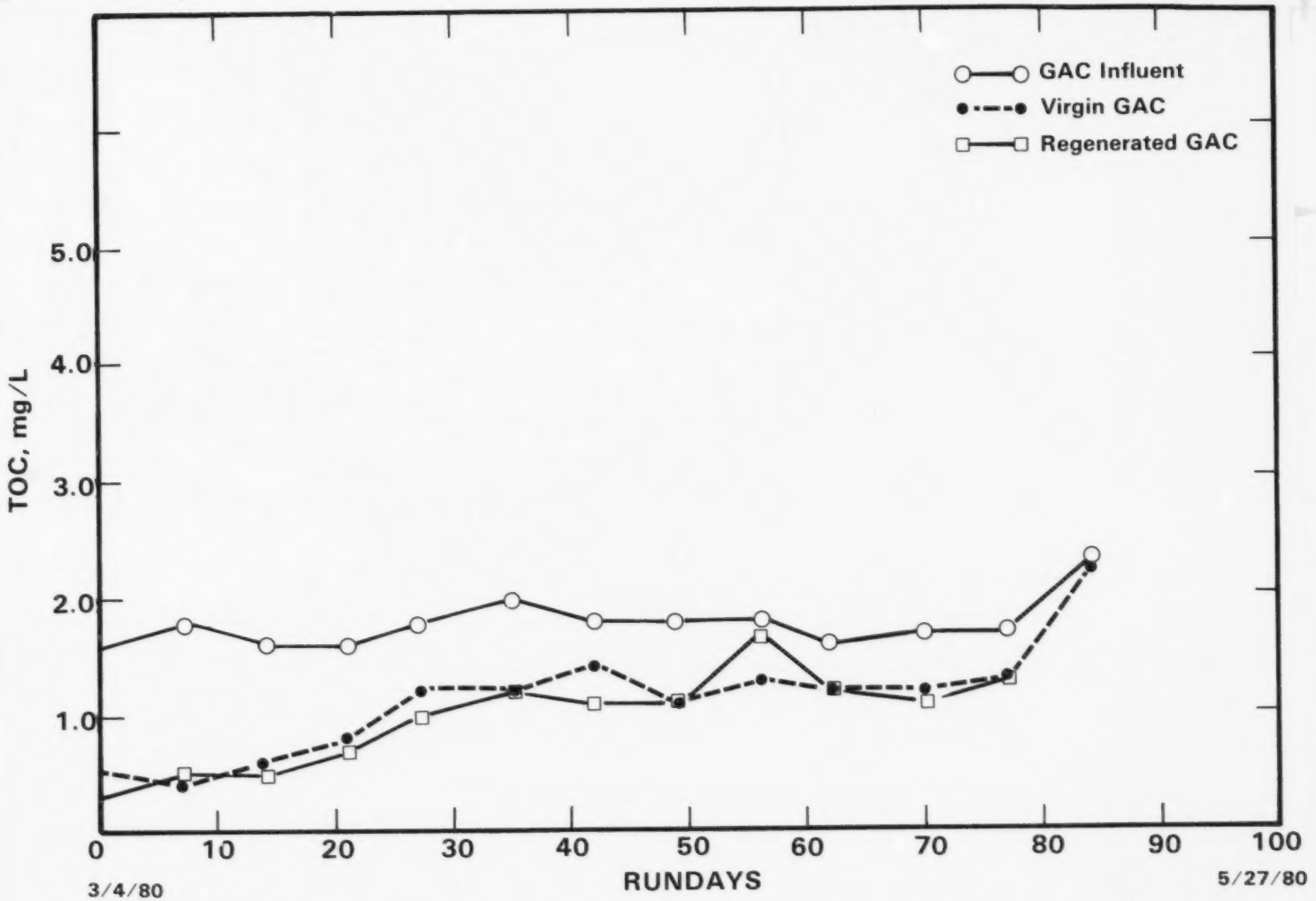

FIGURE 10. COMPARISON OF VIRGIN AND TWICE REACTIVATED GAC - TOC.

from virgin GAC, by evaluating the percent TOC passing, shows that at the beginning of each run this percent was less than 20 for two out of three runs and by day 63 steady-state conditions had occurred for all runs (Figure 13). The percent passing data for the reactivated GAC was less scattered than for the virgin GAC and also visually appears somewhat lower as shown in Figure 14. Less than 20 percent of TOC passed the reactivated GAC at the beginning of each run and as with the virgin GAC, steady-state conditions occurred in about 63 days.

The terminal THM concentration of the effluents from both GAC contactors (virgin and subsequently reactivated) followed each other closely in the first run but were somewhat different in the other two runs (Figures 15, 16, 17). Although the difference in the two effluents was not great, there was some scatter in the data when looking at the virgin and twice reactivated GAC. However, the average effluent terminal THM concentration for both the contactors was essentially the same; virgin was 29.9 ug/L and twice reactivated was 30.1 ug/L. The last run consisting of a comparison of virgin and thrice reactivated GAC showed that the virgin effluent concentration for terminal THM was somewhat less than the reactivated GAC effluent.

The influent concentration for these runs ranged from 18 ug/L in March to 120 ug/L in a September sample. The GAC effluents ranged from not detected (applied concentration 18 ug/L) at the start of a run to about 65 ug/L (applied conentration 62 ug/L) after 85 days of operation.

The inst THM was always low with the applied concentration never exceeding 6 ug/L as shown in Figures 18, 19, and 20. However, as with the control study, the GAC effluent concentration after about 20 days exceeded the applied concentration and in one run (virgin vs once reactivated GAC) actually continued to rise to about 12 ug/L after 85 days of operation. A possibility for this occurrance was noted earlier. The increase in GAC effluent concentration was not as dramatic for the virgin vs twice reactivated GAC. No increase at all was noted when virgin vs thrice reactivated GAC was compared. Regardless of any increase in the concentration of inst THM through the GAC contactors, these concentrations were low, indicating that the THM formation potential for the most part was about the same as the term THM.

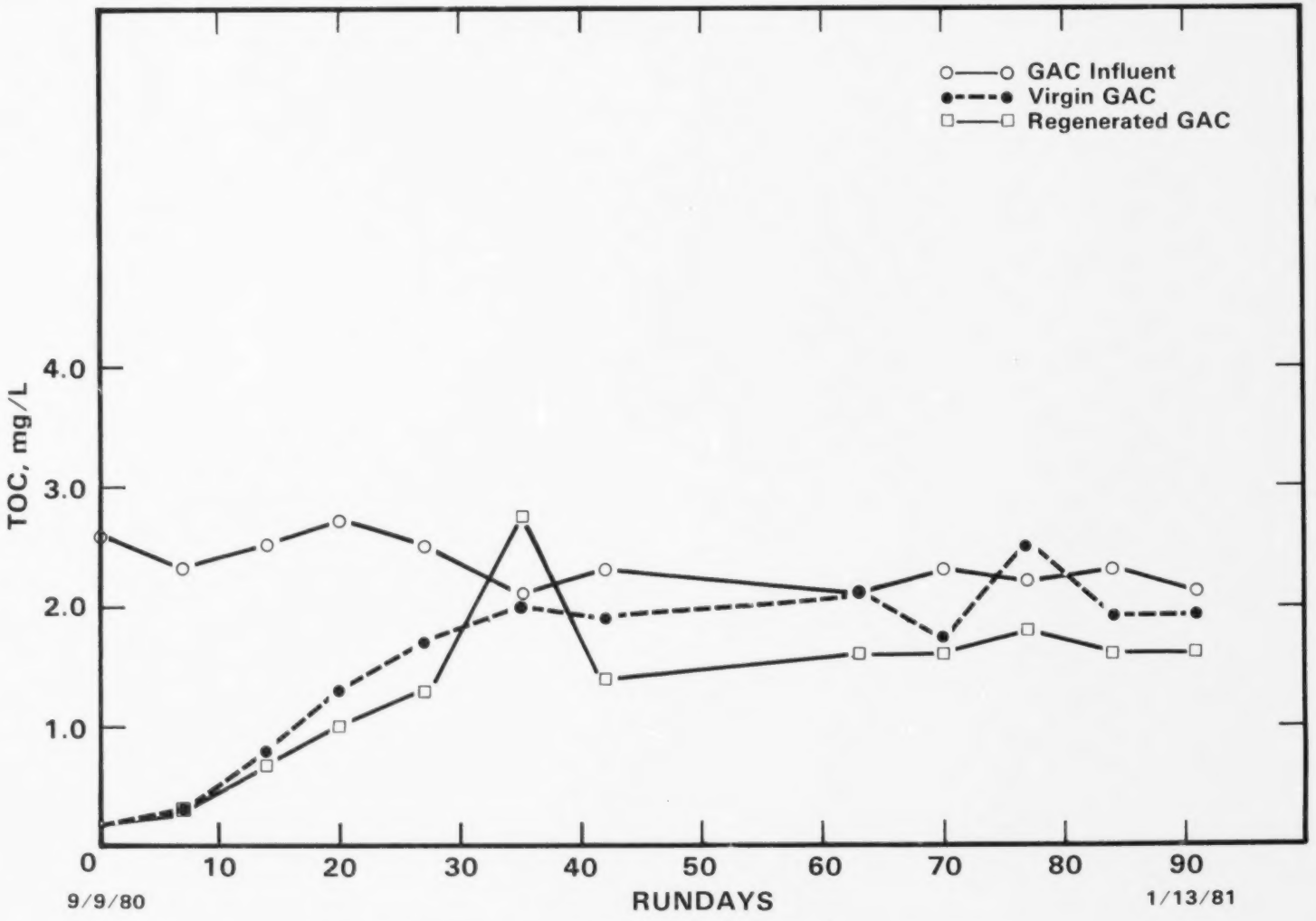

FIGURE 11. COMPARISON OF VIRGIN AND THRICE REACTIVATED GAC - TOC.

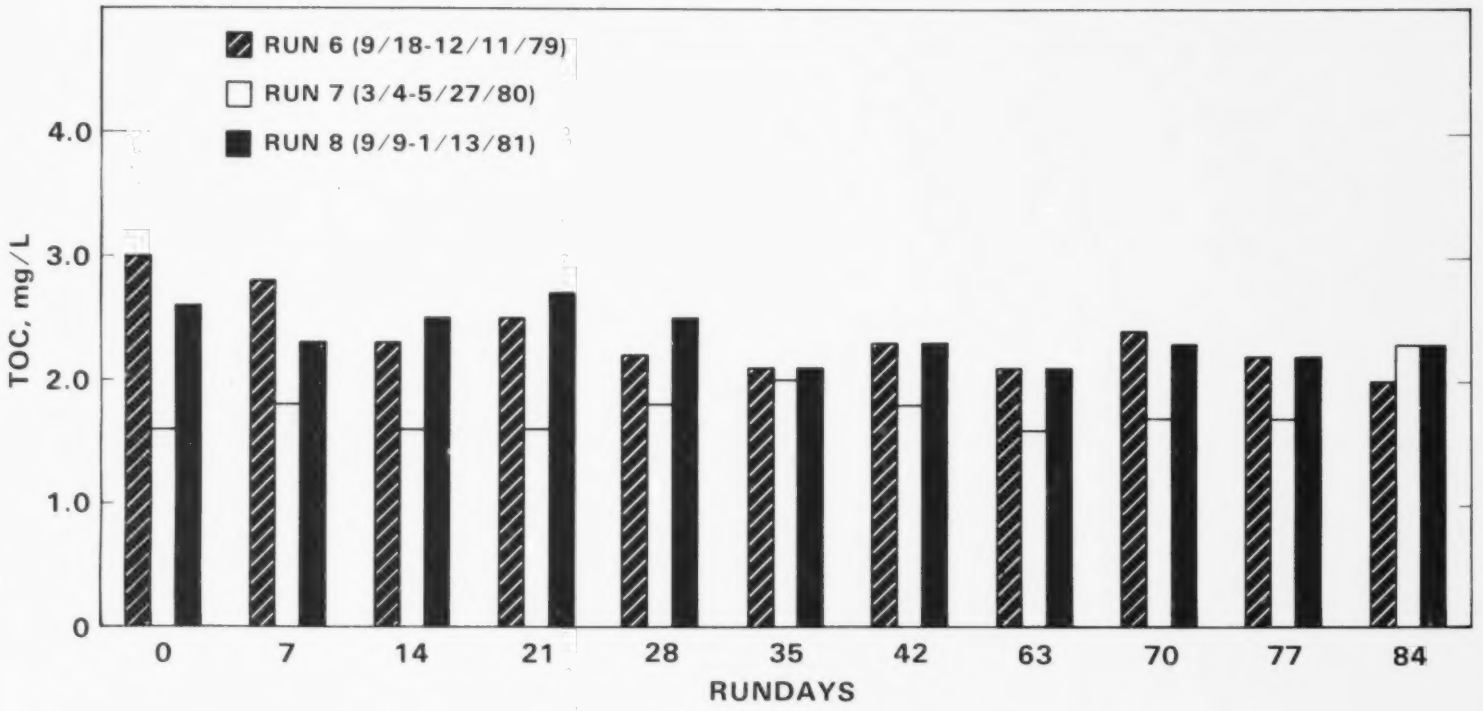

FIGURE 12. TOC CONCENTRATION APPLIED TO GAC CONTACTORS.

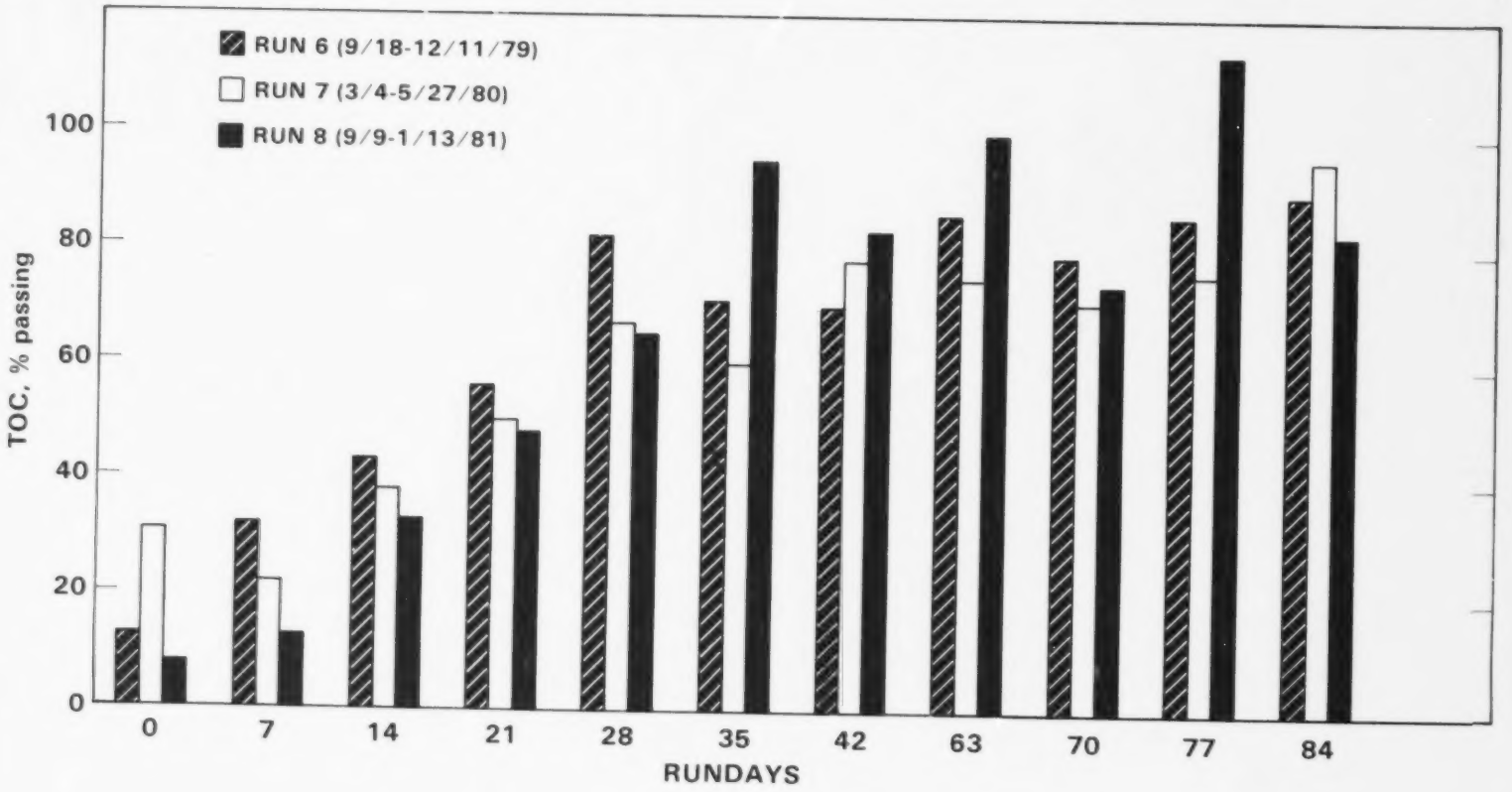

FIGURE 13. PERCENT TOC PASSING THROUGH VIRGIN GAC.

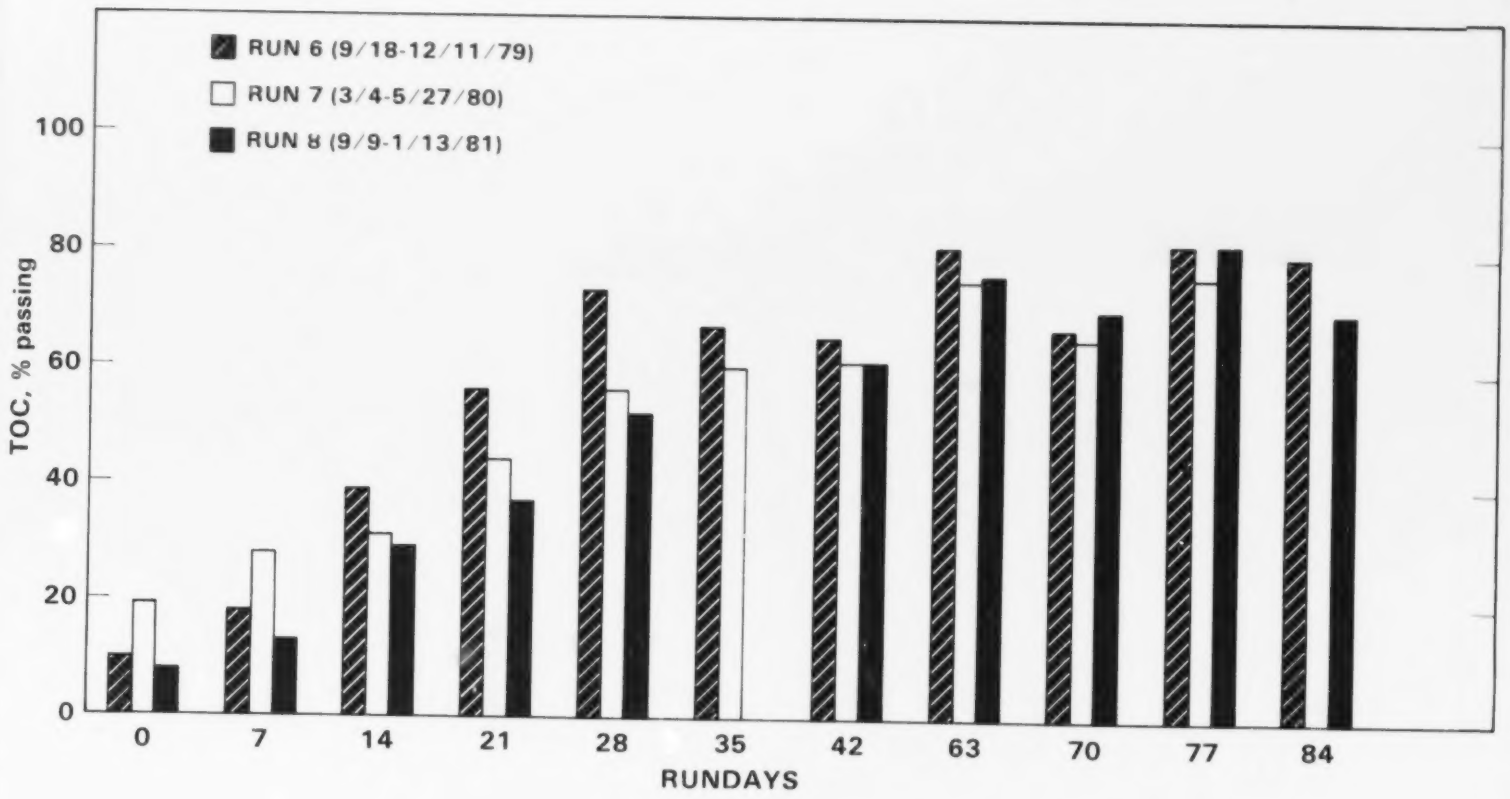

FIGURE 14. PERCENT TOC PASSING THROUGH REACTIVATED GAC.

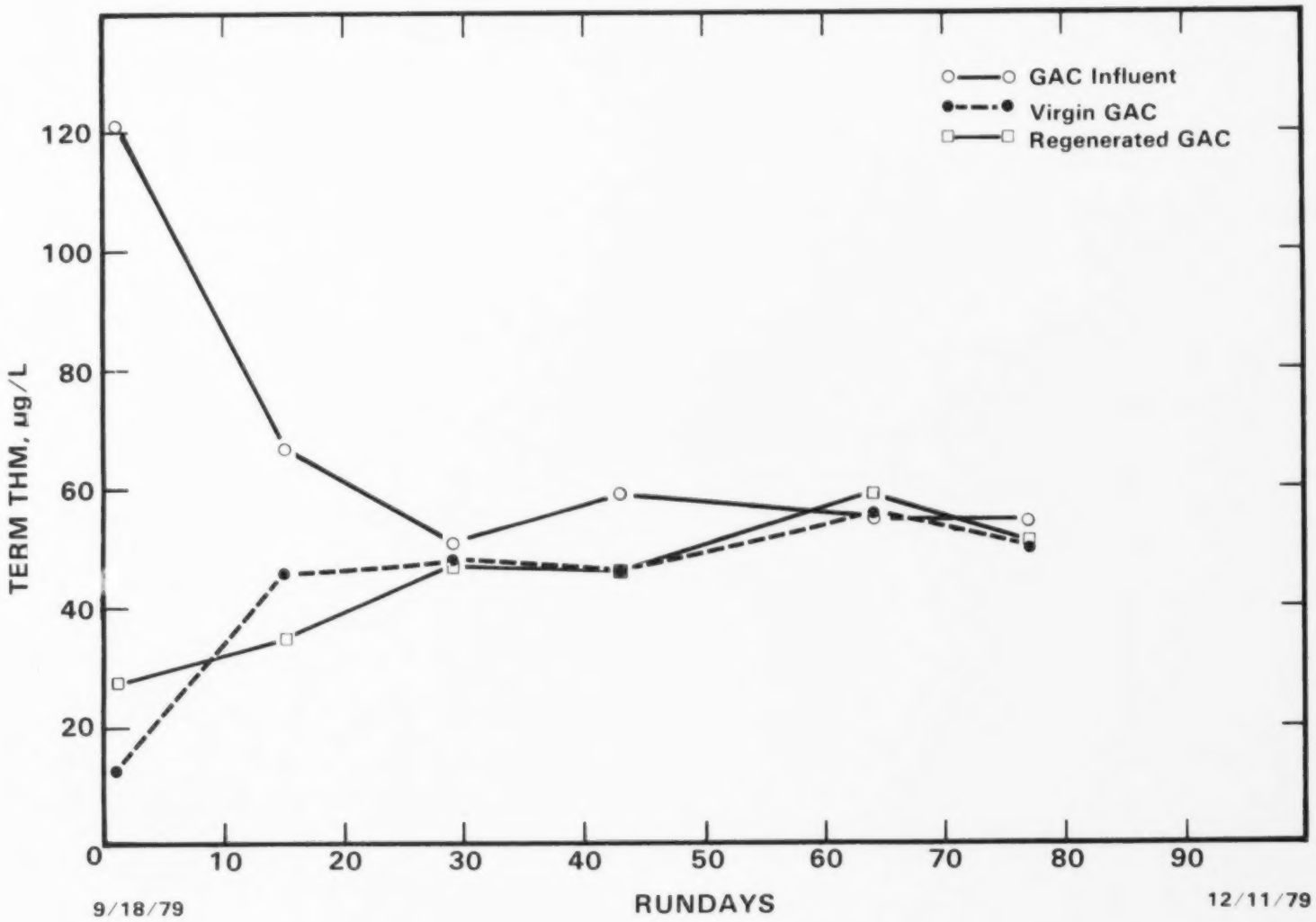

FIGURE 15. COMPARISON OF VIRGIN AND ONCE REACTIVATED GAC - TERM THM.

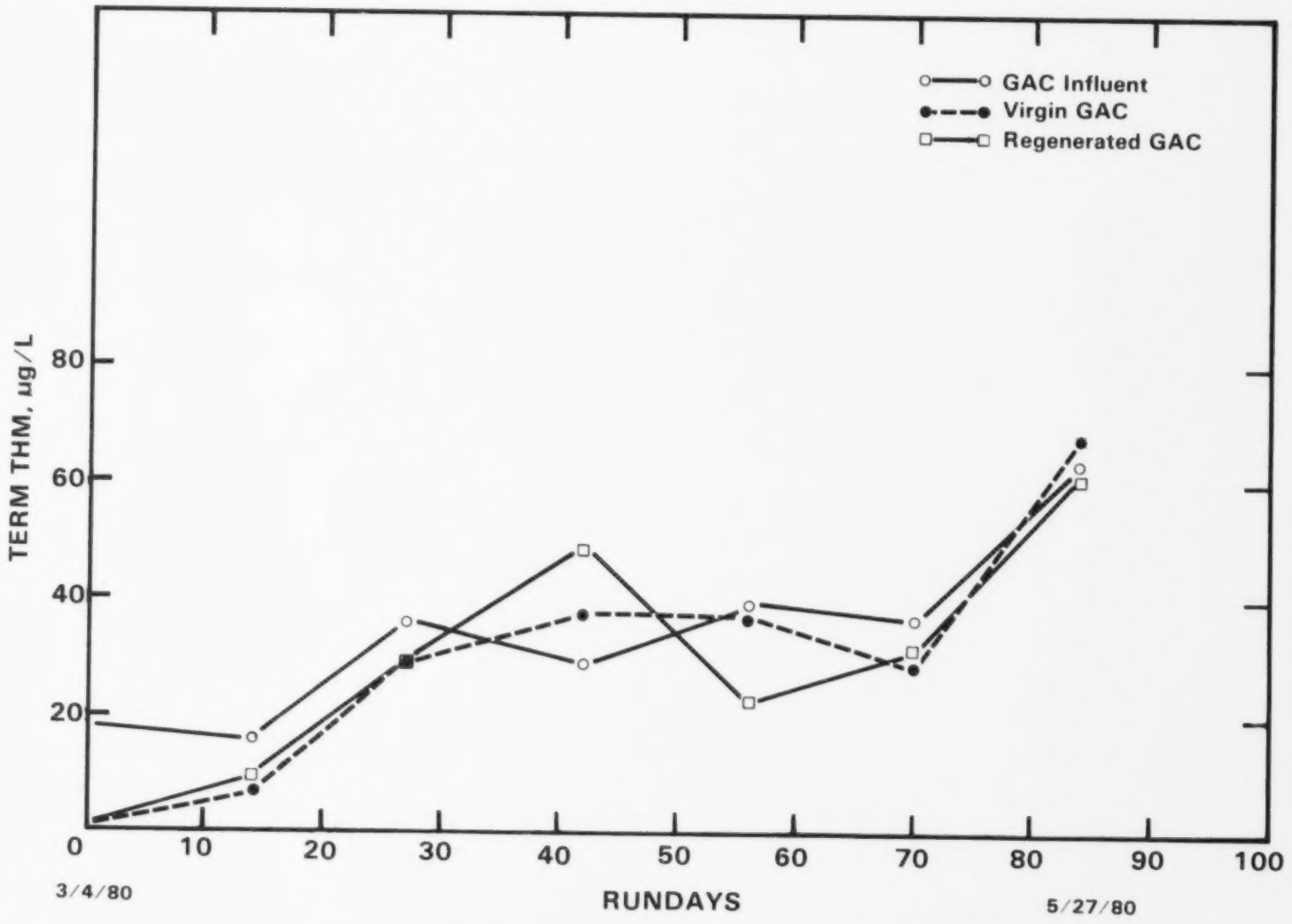

FIGURE 16. COMPARISON OF VIRGIN AND TWICE REACTIVATED GAC - TERM THM.

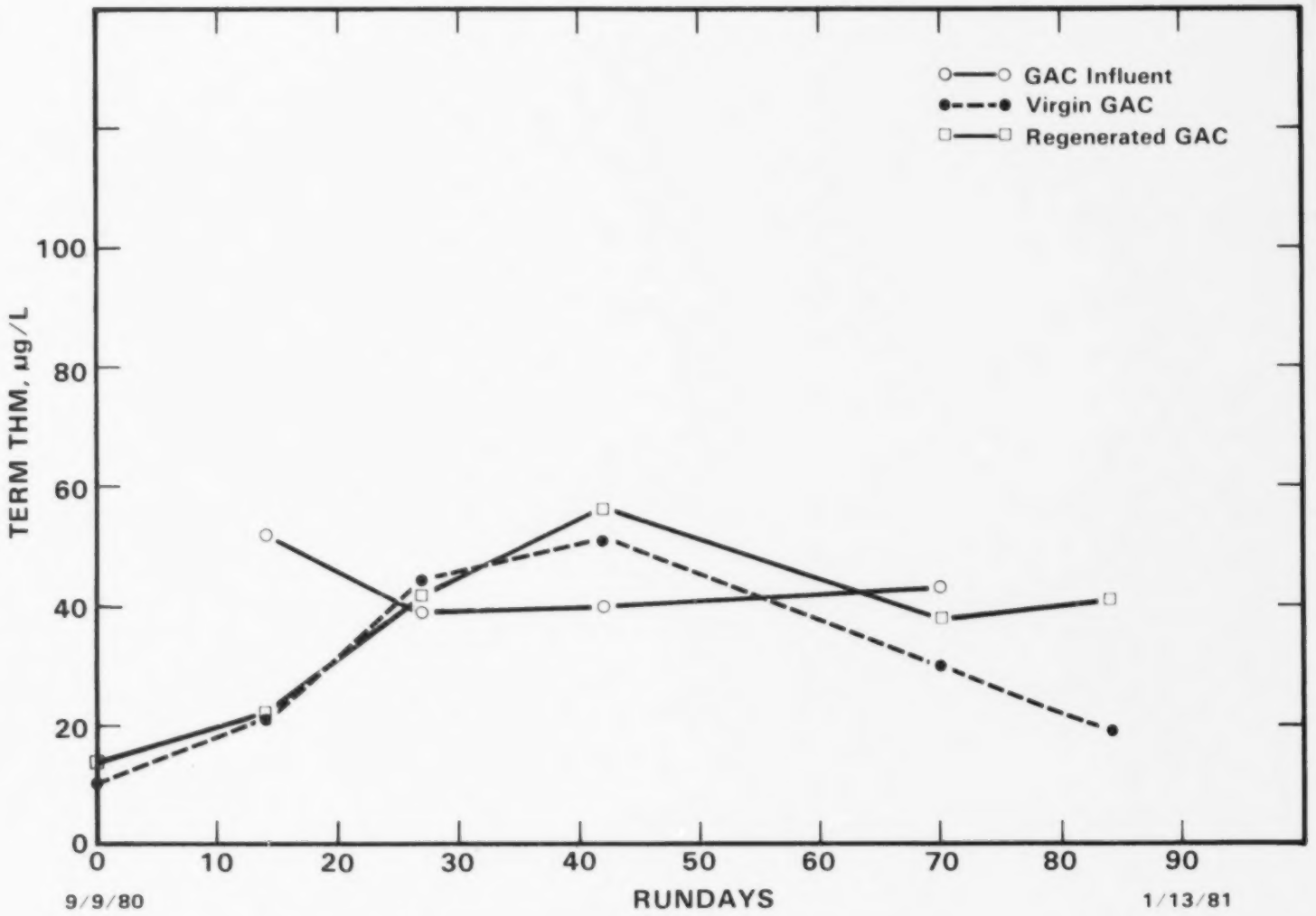

FIGURE 17. COMPARISON OF VIRGIN AND THRICE REACTIVATED GAC - TERM THM.

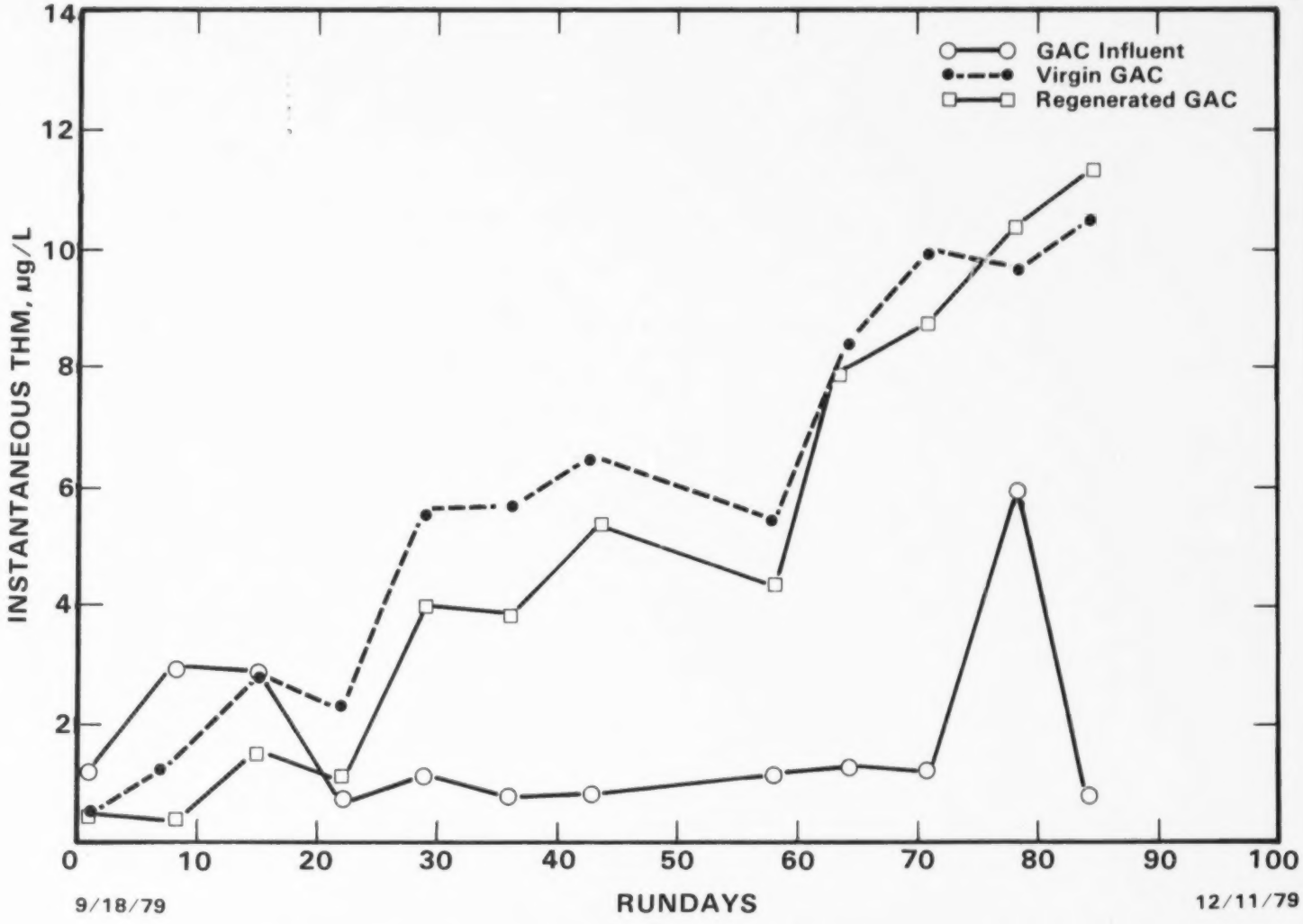

FIGURE 18. COMPARISON OF VIRGIN AND ONCE REACTIVATED GAC - INST THM.

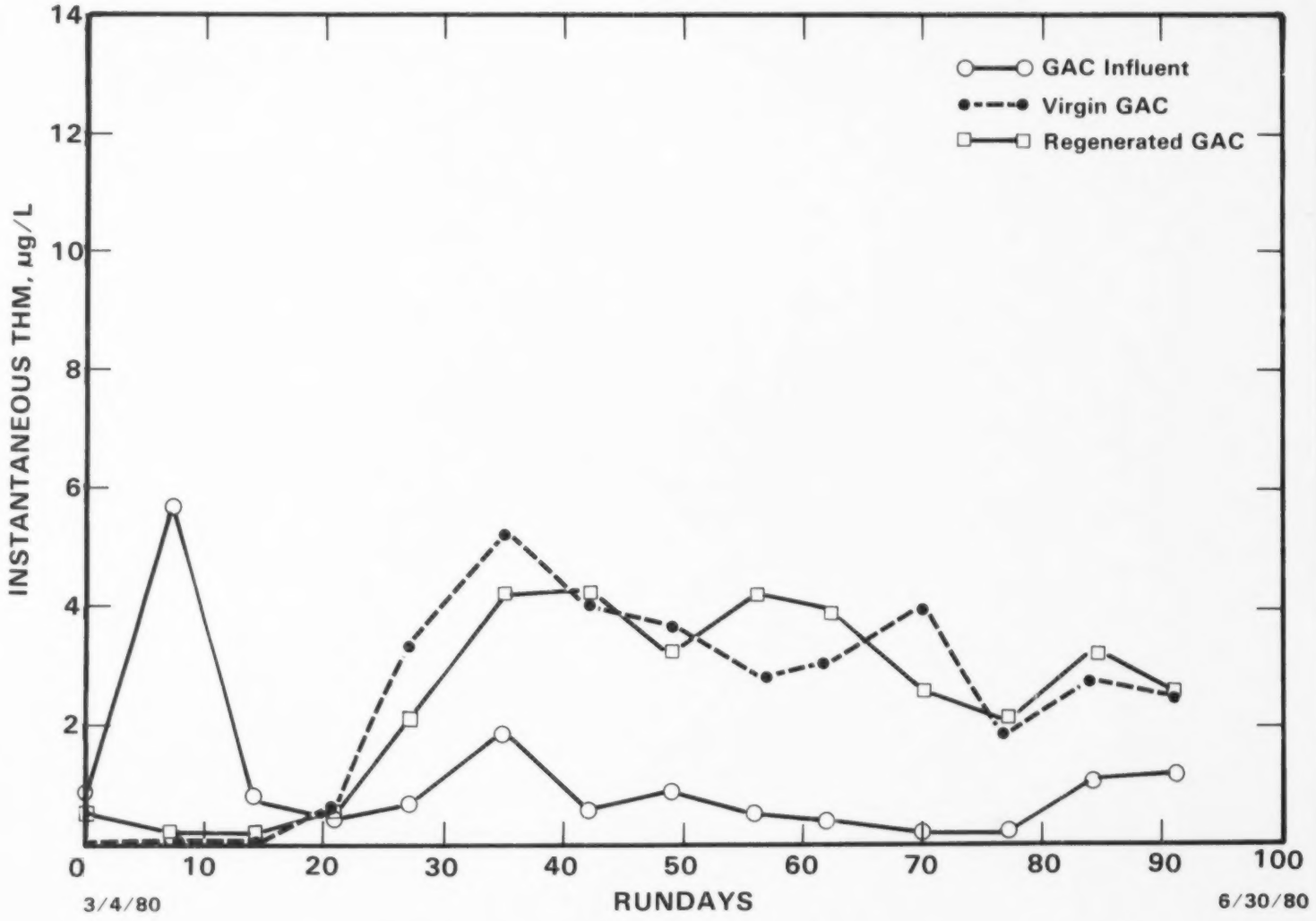

FIGURE 19. COMPARISON OF VIRGIN AND TWICE REACTIVATED GAC - INST THM.

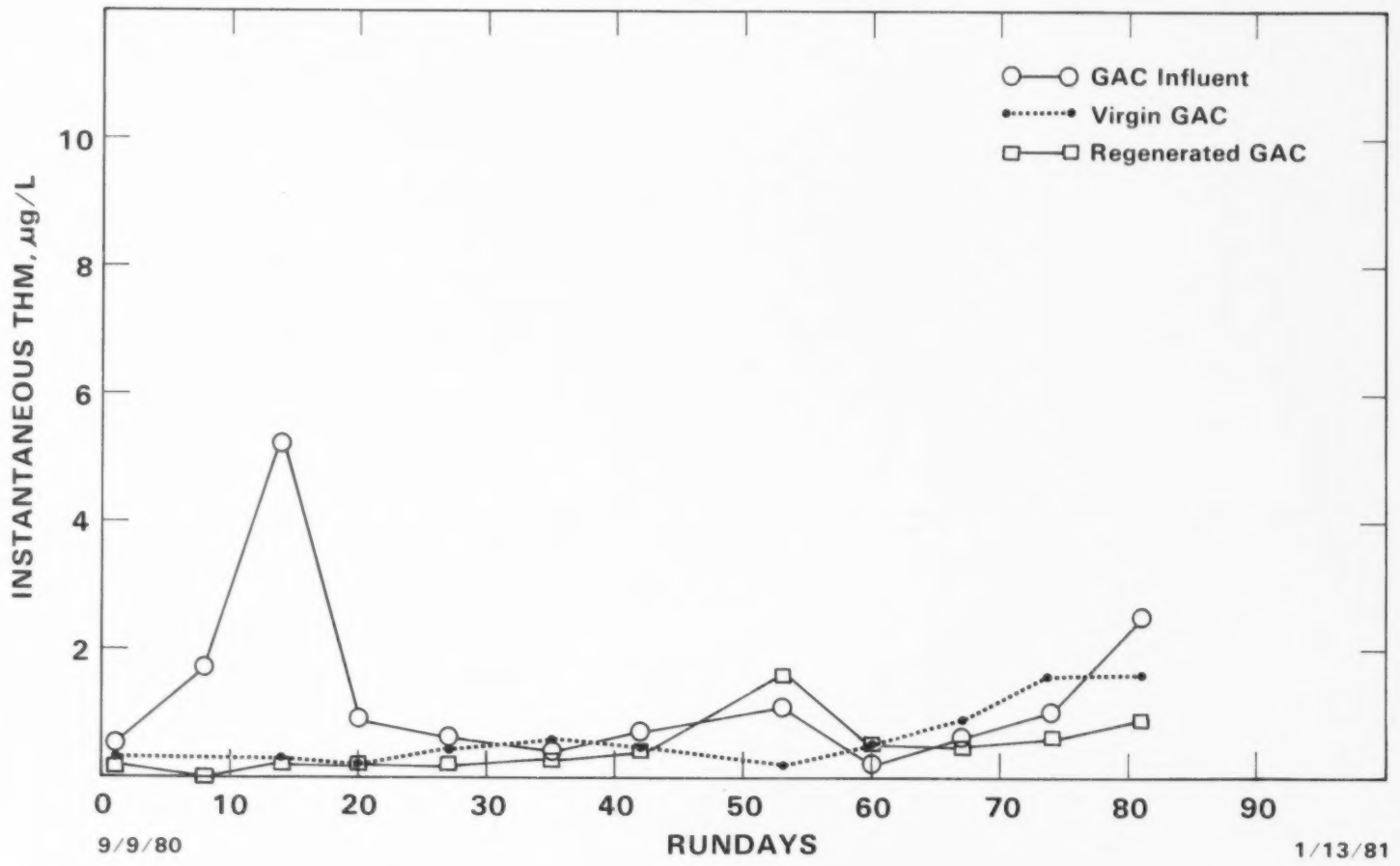

FIGURE 20. COMPARISON OF VIRGIN AND THRICE REACTIVATED GAC - INST THM.

TABLE 21. MINIMUM, MAXIMUM AND AVERAGE TOC CONCENTRATION FOR APPLIED AND GAC EFFLUENT

	Applied TOC Concentration, mg/L		
	Run 6 Vir. vs. 1st React.	Run 7 Vir vs. 2nd React.	Run 8 Vir. vs. 3rd React.
Minimum	2.0	1.6	2.1
Maximum	3.6	2.3	2.7
Average	2.5	1.8	2.3

	GAC Effluent Concentration, TOC in mg/L					
	Run 6		Run 7		Run 8	
	Virgin	1st React.	Virgin	2nd React.	Virgin	3rd React.
Minimum	0.4	0.3	0.4	0.3	0.2	0.2
Maximum	2.4	2.5	2.2	1.7	2.5	2.6
Average	1.5	1.4	1.1	1.0	1.5	1.3

GAC Loading and Carbon Use Rate

Organic loading on the GAC was evaluated for TOC only because of the low concentrations of instantaneous THM and specific organics applied to the GAC. By comparing the two contactors in the control study, the one used for reactivated GAC (T5P) showed less removal than the virgin contactor (T4P) after about 3,000 bed volumes (Figure 21). By normalizing the sum of TOC removed when comparing to the sum of TOC applied, the contactor used for reactivated GAC again showed a slight decrease in the amount of TOC removed when compared to the contactor used for virgin GAC throughout the study as shown in Figure 22.

If one only looked at the bed volumes versus the sum of TOC removed, a wrong conclusion could be drawn. For instance, when the virgin GAC was compared to the once reactivated GAC for bed volumes, the reactivated GAC appeared to remove less TOC (Figure 23). However, when the two contactors were compared on the basis of applied TOC, there was no noticable difference in their performance (Figure 24). In all of the runs, when evaluating the

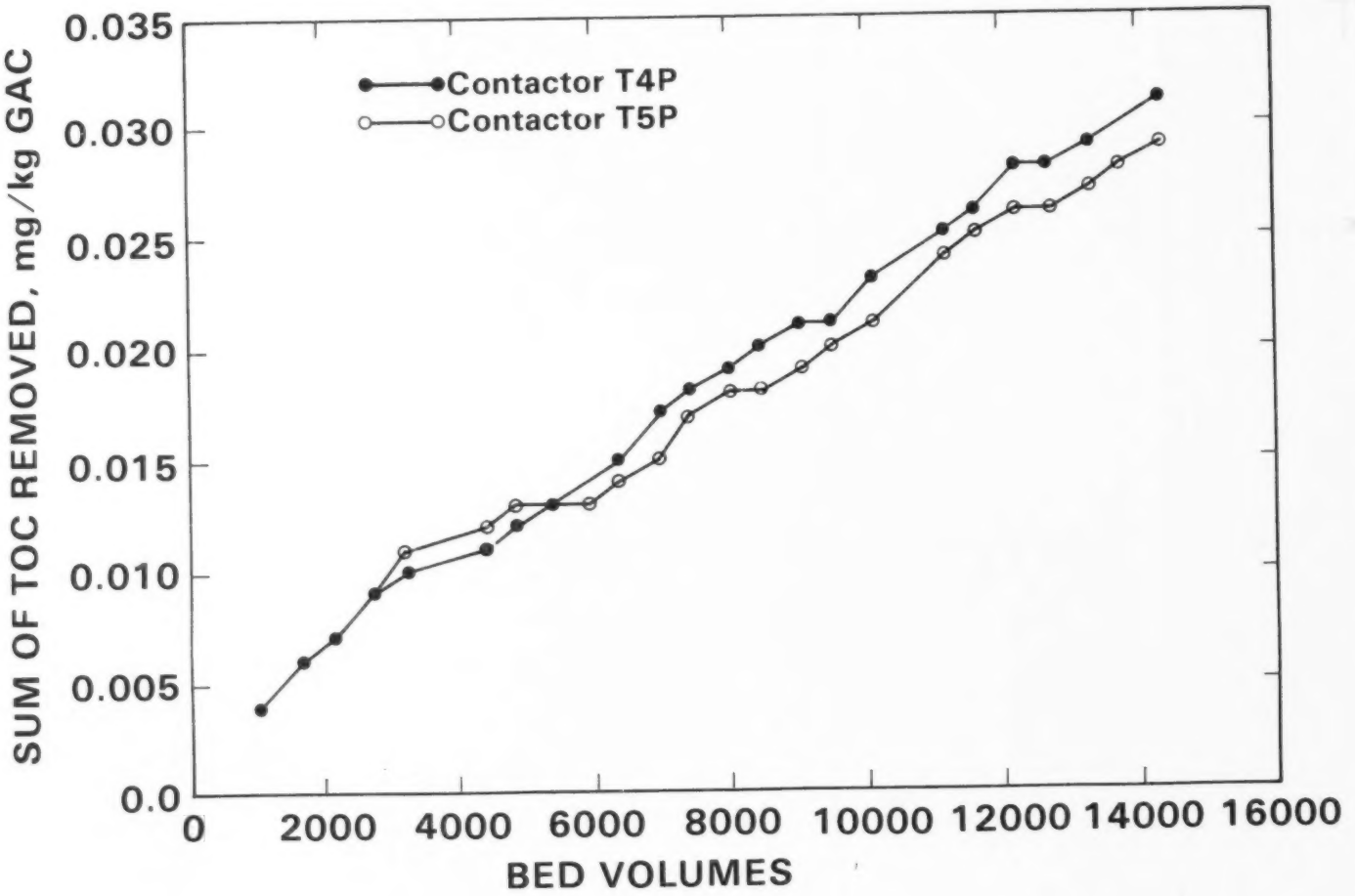

FIGURE 21. CONTROL STUDY - COMPARISON OF TWO CONTACTORS CONTAINING VIRGIN GAC FOR TOC REMOVED VS. BED VOLUME.

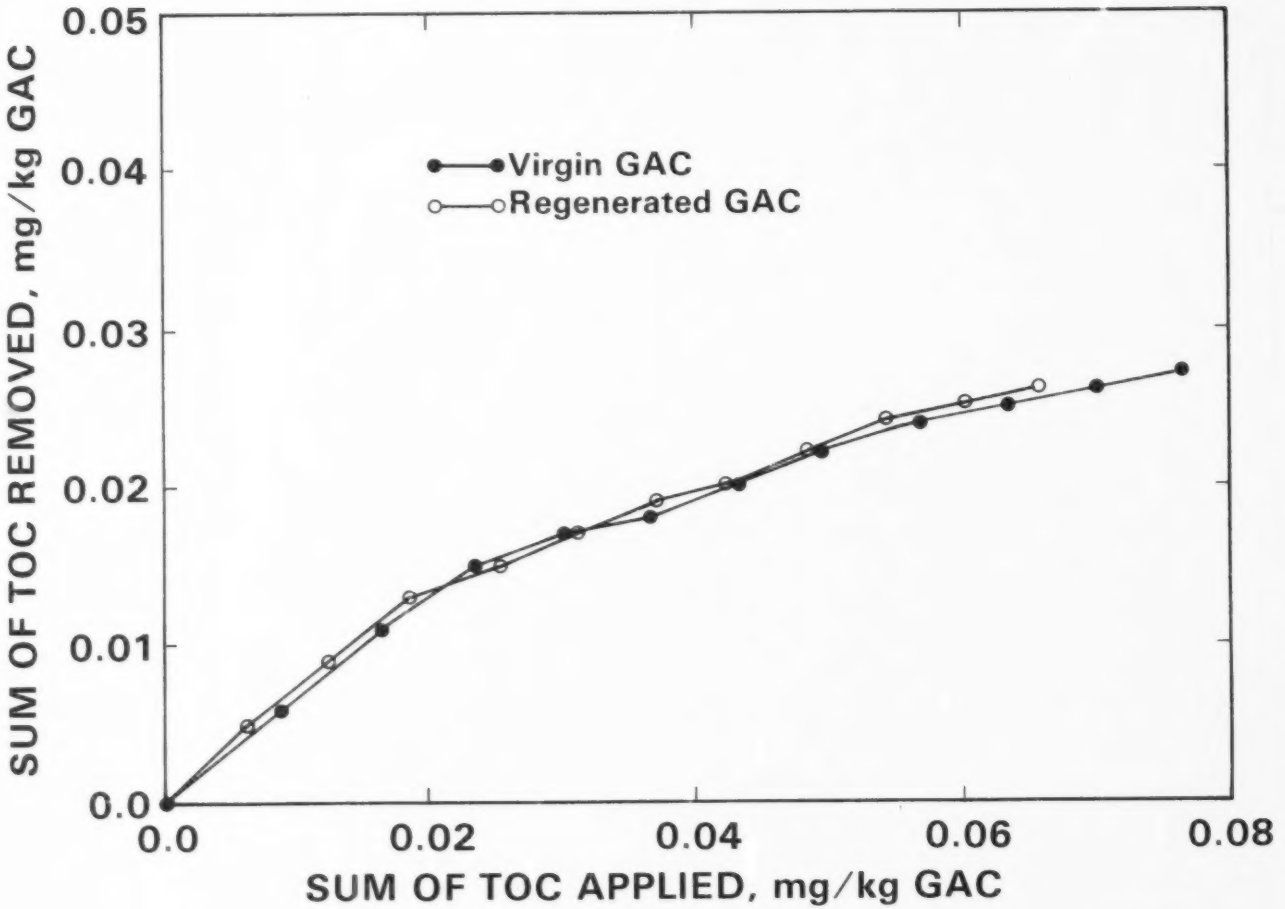

FIGURE 22. CONTROL STUDY - COMPARISON OF TWO CONTACTORS CONTAINING VIRGIN GAC FOR TOC REMOVED VS. TOC APPLIED.

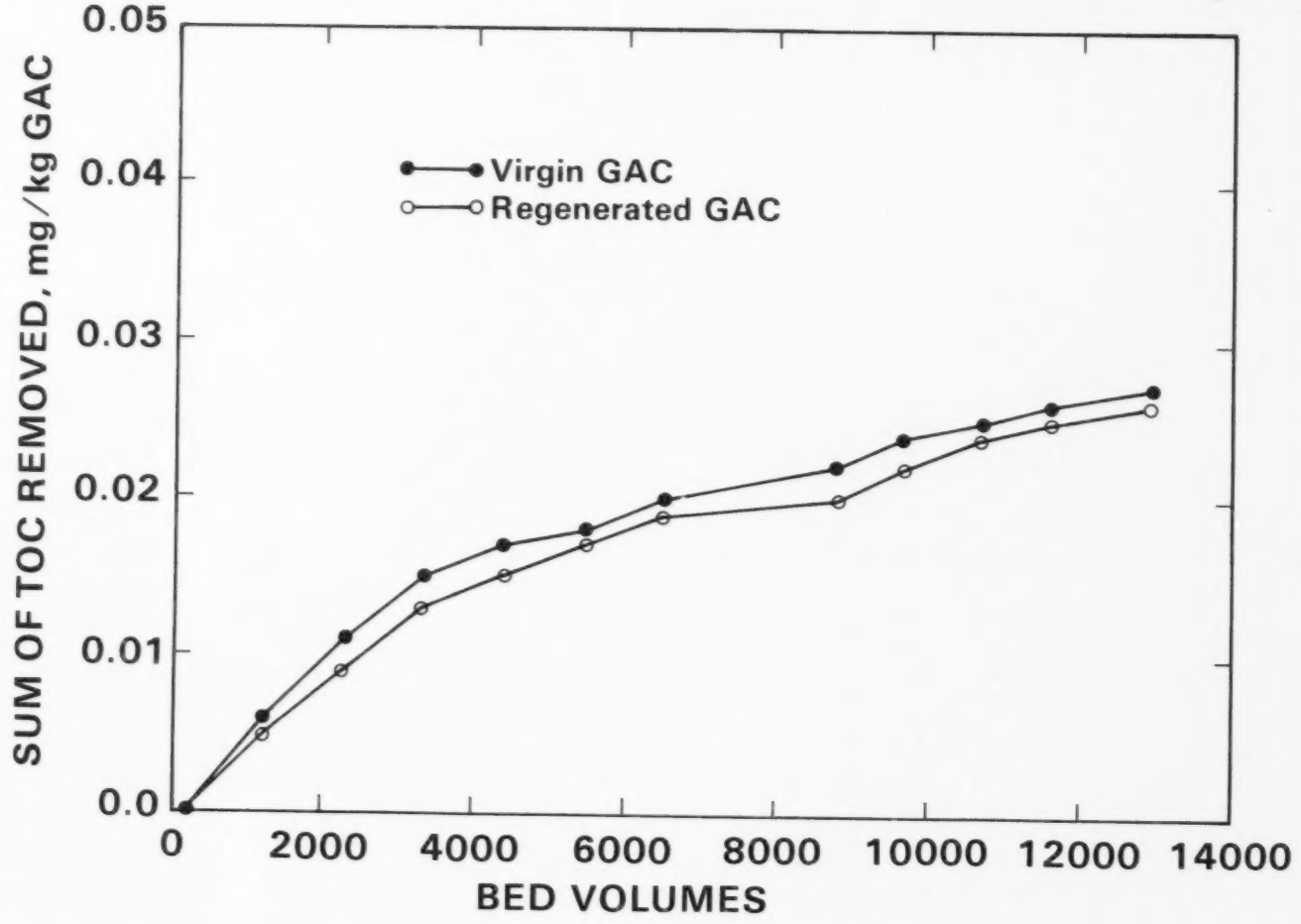

FIGURE 23. COMPARISON OF VIRGIN AND ONCE REACTIVATED GAC FOR TOC REMOVED VS. BED VOLUMES.

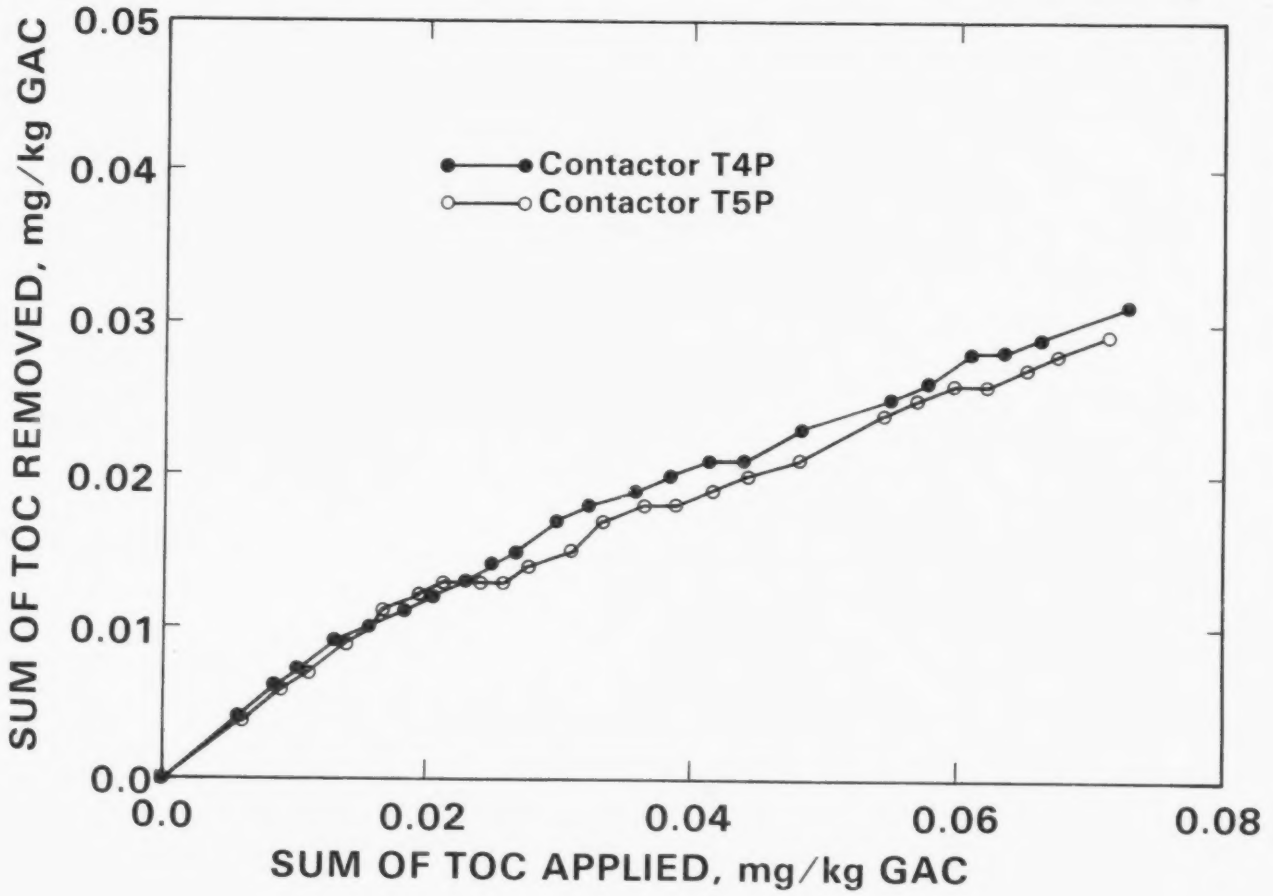

FIGURE 24. COMPARISON OF VIRGIN AND ONCE REACTIVATED GAC FOR TOC REMOVED VS. TOC APPLIED.

TOC removed versus the TOC applied, the virgin and subsequent reactivated GAC was essentially the same indicating similar performance. The average TOC carbon use rate for both the virgin and subsequent reactivated GAC was about 0.05 kg/m^3 at steady state conditions that occurred after about 60 days of operation (Figure 25).

COMPARISON OF GAC CONTACTORS FOR PARAMETERS OTHER THAN TOC AND THM

Total Coliform, SPC, and Speciation

In any study where the normally used disinfectant is changed, there is some concern about the bacteriological quality of the water after treatment. During this study samples were collected for in-plant analyses of the standard plate count (SPC) and total coliform. The average raw water SPC for all the runs ranged from 1,500 to 6,300/mL. Chlorine dioxide application to the raw water reduced this average range to 1-80/mL after mixed media filtration (GAC influent). The larger average concentration of 80/mL was seen when the influent concentration was the highest (6,300/mL) as shown in Table 22.

For all of the long-term runs during this study, the effluent from the virgin GAC was always higher in SPC than the effluent from the reactivated GAC. However, no reason can be postulated for this difference because when virgin GAC was placed in both contactors, a higher SPC value was seen in the contactor effluent that always received virgin GAC. In all cases there was a regrowth of SPC through both GAC contactors. By the addition of 1-1.5 mg/L of chlorine dioxide to the GAC effluent, the SPC was reduced to an average of 2-8/mL depending on the run.

The average total coliform of the raw water to the pilot plant averaged from 1,400 to 31,500/100 mL for the four runs and at one point ran as high as 990,000/100 mL. As with the SPC, these numbers were reduced to an average range of 0-7/100 mL after mixed media filtration. Ideally, the total coliforms should have been zero in all cases after application of chlorine dioxide. In a full scale plant with longer detention and contact time, this would most likely have occurred. In contrast to the SPC, the total coliform concentration through the GAC contactors actually decreased where there was some applied to the GAC as shown in Table 23. Post GAC disinfection with chlorine dioxide reduced all total coliform values to less than one.

In conjunction with the SPC and total coliforms, some speciation was attempted. At the time that samples were collected, the intent was to isolate and identify the various species present in the GAC influent and the effluent from both contactors. The samples were sent to the Microbiological Treatment Branch of the Drinking Water Research Division, U.S. EPA, Cincinnati, Ohio for analysis.

By using an R-2A medium[12] (several nutrients in low concentrations) pigmented bacteria were isolated. Most of the effluent water from both the virgin and reactivated GAC contained some pigmented bacteria. This occurred even though the influent to the GAC contactors sometimes showed no significant pigmented bacterial populations during periods when increased concentrations of chlorine dioxide were applied to the raw water to maintain a residual of 0.3 to 0.5 mg/L in the GAC influent. At other times, when a few pigmented

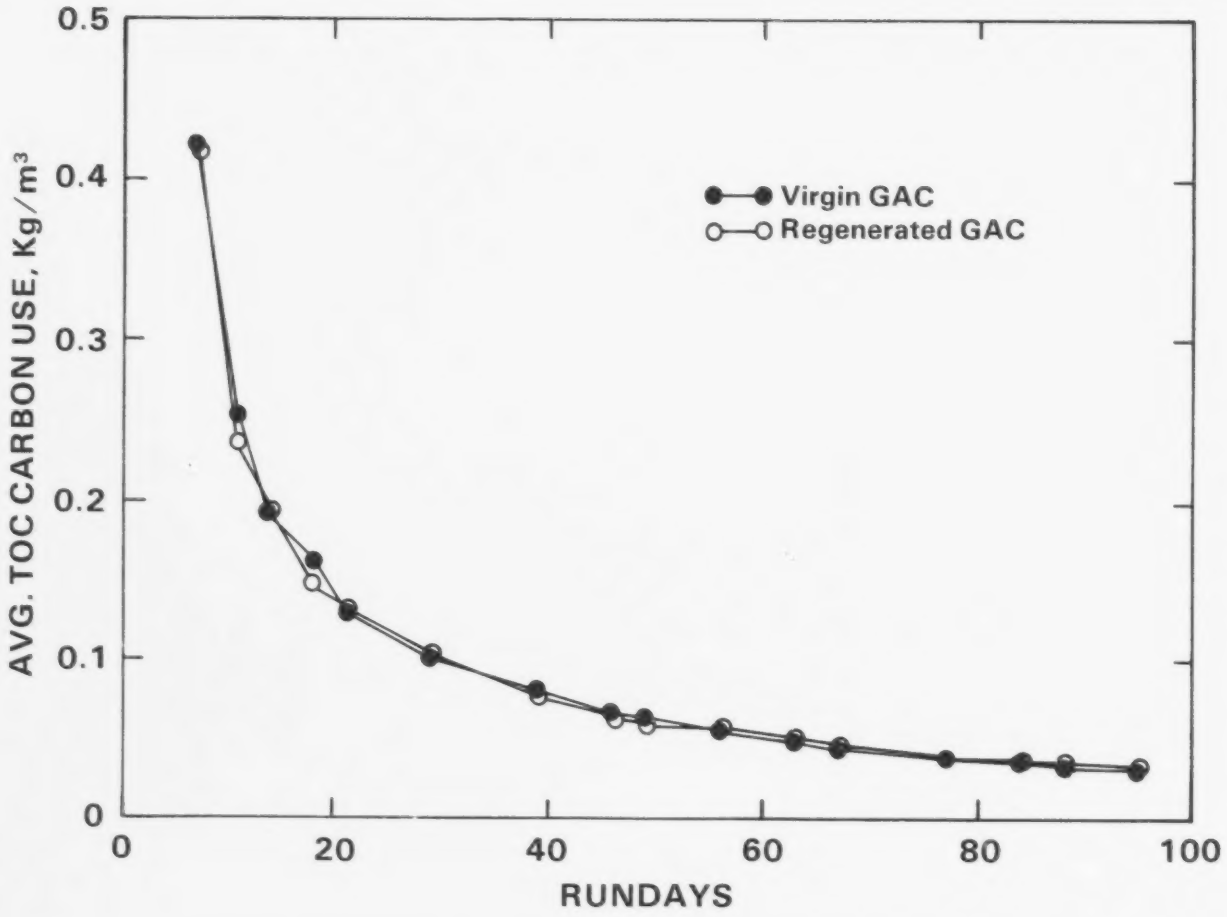

FIGURE 25. COMPARISON OF VIRGIN AND REACTIVATED GAC - AVERAGE CARBON USE FOR TOC.

bacteria were seen in the source water, essentially none were noticed in the GAC contactor effluents.[10] Identification of these pigmented bacteria was difficult and was attempted to some degree as an additional research effort without much success.

TABLE 22. MINIMUM, MAXIMUM, AND AVERAGE SPC VALUES

RUN	DATE	RAW WATER (#/mL)	PILOT PLANT EFFLUENT (GAC INF.) (#/mL)	VIRGIN GAC CONTACTOR (#/mL)	REACTIVATED GAC CONTACTOR (#/mL)
5(1)	4/23 - 7/23/79				
min.		12	ND	ND	ND
max.		40,000	1,100	17,000	8,000
avg.		3,800	60	770	400
6(2)	9/18 - 12/11/79				
min.		200	ND	ND	ND
max.		27,000	1,000	9,800	6,600
avg.		6,300	80	630	330
7(3)	3/4 - 6/30/80				
min.		300	ND	ND	ND
max.		8,900	35	300	160
avg.		1,700	1	15	12
8(4)	9/9/80 - 1/13/81				
min.		400	ND	ND	ND
max.		7,000	50	15,000	8,800
avg.		1,500	4	1,200	550

(1) Run 5 - Virgin GAC in Both Contactors
(2) Run 6 - Virgin GAC in One Contactor - Once Reactivated GAC in Other Contactor
(3) Run 7 - Vigin GAC in One Contactor - Twice Reactivated GAC in Other Contactor
(4) Run 8 - Virgin GAC in One Contactor - Thrice Reactivated GAC in Other Contactor

TURBIDITY, pH, AND TEMPERATURE

As stated previously, a polymer was added to the pilot plant to effect turbidity removal consistent with the full-scale plant. In the original control

study lasting only two weeks, the turbidity in both plants was essentially the same. For the long-term runs, this was still the case as shown in Table 24. Passage of the water through GAC removed some additional turbidity.

The pH in the pilot plant ranged from 6.6 to 8.9. In the full scale plant it varied from 7.0 to 8.5. Lime was utilized in both plants for pH control. The temperature of the water in both plants varied depending on the season with an average range of 12.6 to 22.1°C.

Metals

There has been some concern that certain heavy metals leach from virgin GAC and will be seen in the effluent. Under stressed conditions such as acid refluxing or continuous distilled water recyclying quantifiable amounts of some metals have been leached from GAC.[13] With the natural surface water source at Evansville, little if any increased concentration of the metals was detected in the GAC effluent as compared to the influents as shown in Table 25.

The data in this table shows that only a few of the 8 metals (MCL's) analyzed for each run were somewhat higher in the effluent concentration than the influent. In evaluating the data, there is a high probability that any difference noted was caused by analytical error. At sometime during the study, all of the metals except cadmium were detected, in low concentrations, in the raw water. Coagulation/settling treatment either completely removed or reduced most of these concentrations.

Two other metals without MCLs were also analyzed. These were iron and manganese. The highest concentrations for these two metals seen in the raw water was 4.5 and 1.5 mg/L, respectively, for iron and manganese. Concentrations of both of these parameters were reduced to essentially zero after coagulation/settling.

TABLE 23. MINIMUM, MAXIMUM, AND AVERAGE TOTAL COLIFORM VALUES

RUN	DATE	RAW WATER (#/100 mL)	PILOT PLANT EFFLUENT (GAC. INF.) #/100 mL	VIRGIN GAC CONTACTOR #/100 mL	REACTIVATED GAC CONTACTOR #/100 mL
5(1)	4/23 - 7/23/79				
min.		600	ND	ND	ND
max.		990,000	60	50	55
avg.		31,500	4	1	1
6(2)	9/18 - 12/11/79				
min.		1,600	ND	ND	ND
max.		112,000	40	58	8
avg.		17,600	7	2	1
7(3)	3/4 - 6/30/80				
min.		500	ND	ND	ND
max.		23,000	ND	2	ND
avg.		2,900	ND	ND	ND
8(3)	9/9/80 - 1/13/81				
min.		300	ND	ND	ND
max.		3,700	1	4	1
avg.		1,400	ND	ND	ND

(1) Run 5 - Virgin GAC in Both Contactors
(2) Run 6 - Virgin GAC in One Contactor - Once Reactivated GAC in Other Contactor
(3) Run 7 - Virgin GAC in One Contactor - Twice Reactivated GAC in Other Contactor
(4) Run 8 - Virgin GAC in One Contactor - Thrice Reactivated GAC in Other Contactor

TABLE 24. MINIMUM, MAXIMUM, AND AVERAGE TURBIDITY

RUN	DATE	RAW WATER (NTU)	PILOT PLANT EFFLUENT (GAC INF.) (NTU)	FULL-SCALE PLANT EFFLUENT (NTU)
5(1)	4/23 - 7/23/79			
min.		14	0.15	0.08
max.		150	3.2	1.2
avg.		43	0.27	0.22
6(2)	9/18 - 12/11/79			
min.		18	0.17	0.18
max.		350	24	0.70
avg.		87	1.1	0.33
7(3)	3/4 - 6/30/80			
min.		20	0.15	0.16
max.		175	1.0	0.64
avg.		85	0.30	0.23
8(4)	9/9/80 - 1/13/81			
min.		7.0	0.20	0.14
max.		58	7.0	0.50
avg.		21	0.75	0.22

(1) Run 5 - Virgin GAC in Both Contactors
(2) Run 6 - Virgin GAC in One Contactor - Once Reactivated GAC in Other Contactor
(3) Run 7 - Virgin GAC in One Contactor - Twice Reactivated GAC in Other Contactor
(4) Run 8 - Virgin GAC in One Contactor - Thrice Reactivated GAC in Other Contactor

TABLE 25. INSTANCES WHERE AVERAGE METAL CONCENTRATION IN GAC EFFLUENT EXCEEDED INFLUENT

PARAMETER	GAC INFLUENT	VIRGIN GAC EFFLUENT	REACTIVATED GAC EFFLUENT	COMMENTS
Barium	0.00	0.12	0.00	Run 5
Barium	0.05	0.13	0.08	Run 6
Lead	0.01	0.01	0.02	Run 6
Arsenic	0.000	0.000	0.004	Run 6
Selenium	0.000	0.003	0.000	Run 6
Selenium	0.000	0.003	0.000	Run 7

FATE OF CHLORINE DIOXIDE AND CHLORITE IN THE PILOT PLANT

The fate of chlorine dioxide and one of its inorganic species (chlorite) varied during treatment. In generating chlorine dioxide, a stoichiometric reaction was not possible thereby introducing an average of 0.7 mg/L of chlorite and 0.2 mg/L of chlorine when an average dose of 1.6 mg/L of chlorine dioxide was applied to the raw water. During conventional treatment (coagulation/settling/filtration), the chlorine dioxide concentration decreased but the chlorite concentration increased as shown in Table 26. Additional treatment by GAC adsorption reduced the chlorite concentration and completely removed the chlorine dioxide. Therefore, additional chlorine dioxide was added after GAC treatment for disinfection.

At the time of this study, useable methods for determining chlorine dioxide were scarce. A modification of the DPD-FAS titrimetric method developed by Palin as described in the 13th edition of Standard Methods was selected because it was the only known method that would also permit chlorite determinations.[2,14,15] Because of our uncertainity as to the reliability of this method, a search was conducted to try to find another method that could be used in a plant laboratory for comparison.[16-23]

The method selected for comparison to the titrimetric DPD-FAS method was the chlorophenol red (CPR) method.[22] Only chlorine dioxide could be determined with this method and no method could be found to evaluate DPD-FAS for chlorite. By evaluating the average concentrations of chlorine dioxide in Table 27 for all runs, the two methods showed comparable results.

TABLE 26. AVERAGE CONCENTRATION OF CHLORINE DIOXIDE AND CHLORITE THROUGH PILOT PLANT TREATMENT

RUN	APPLIED TO RAW WATER mg/L	PILOT PLANT EFFLUENT (GAC INFLUENT) mg/L	VIRGIN GAC EFFLUENT mg/L	REACTIVATED GAC EFFLUENT mg/L	POST GAC EFFLUENT mg/L
5(1)					
ClO_2	1.5	0.4	ND	ND	1.1
ClO^-_2	0.5	2.5	0.4	0.4	0.8
6(2)					
ClO_2	1.4	0.4	ND	ND	0.9
ClO^-_2	1.2	-	0.1	0.1	0.6
7(3)					
ClO_2	1.7	0.8	ND	ND	0.9
ClO^-_2	0.8	2.8	1.0	1.0	1.6
8(4)					
ClO_2	1.7	1.1	ND	ND	1.4
ClO^-_2	0.2	1.2	0.9	0.8	0.9

(1) Run 5 - Virgin GAC in Both Contactors
(2) Run 6 - Virgin GAC in One Contactor - Once Reactivated GAC in Other Contactor
(3) Run 7 - Virgin GAC in One Contactor - Twice Reactivated GAC in Other Contactor
(4) Run 8 - Virgin GAC in One Contactor - Thrice Reactivated GAC in Other Contactor

TABLE 27. COMPARISON OF AVERAGE CHLORINE DIOXIDE CONCENTRATION FOR DPD-FAS AND CPR METHODS

RUN	PILOT PLANT EFFLUENT		POST GAC EFFLUENT	
	DPD-FAS (mg/L)	CPR (mg/L)	DPD-FAS (mg/L)	CPR (mg/L)
5(1)	0.4	0.6	1.1	1.1
6(2)	0.4	0.4	0.9	0.7
7(3)	0.8	0.8	0.9	0.9
8(4)	1.1	1.1	1.4	1.2

(1) Run 5 - Virgin GAC in Both Contactors
(2) Run 6 - Virgin GAC in One Contactor - Once Reactivated GAC in Other Contactor
(3) Run 7 - Virgin GAC in One Contactor - Twice Reactivated GAC in Other Contactor
(4) Run 8 - Virgin GAC in One Contactor - Thrice Reactivated GAC in Other Contactor

THM EFFECT OF RAW WATER DISINFECTION WITH CHLORINE DIOXIDE

During this study, the effectiveness of both chlorine and chlorine dioxide was comparable. Historically, chlorine has been used in the United States for many years as the major disinfectant in water treatment plants. Its disinfectant quality is beyond reproach. However, recently, alternate disinfectants have been more widely considered and the disinfectant quality of chlorine dioxide has been well documented.[24-29]

As stated previously, the full-scale plant adding chlorine to the raw water and sand filter effluent was used as a control for comparison to the pilot plant that added chlorine dioxide to the raw water and GAC effluent. By comparing the filter effluents of both plants in relation to the raw water influent, a determination of the effect of using pre-chlorine dioxide disinfection for the reduction of THMs was evaluated.

In order to effectively evaluate the reduction of THMs by pre-chlorine dioxide disinfection, precursor removal through coagulation/settling was determined by storing all samples for 3 days (estimate of residence time in distribution system) with a free chlorine residual. This procedure gave the terminal THM values which were used to compare the two disinfectant treatment systems. By comparing the terminal THMs, an indication as to what one might expect in the distribution system was established.

Figure 25 gives a visual perspective as to the reduced concentration of terminal THMs that were noticed when raw water chlorine dioxide disinfection was used. As shown in this figure, the use of pre-chlorine dioxide disinfection allowed substantially more of the THM precursors to be removed by coagulation/settling than with prechlorination, thereby reducing the amount of THMs formed during post-treatment chlorination and subsequently in the distribution system. An overall average comparison of the terminal THM concentration for all runs when evaluating the two disinfectant modes showed about 60 percent less when chlorine dioxide was used. Although THM precursors were reduced by using pre-chlorine dioxide, no difference was noted in the average TOC concentration regardless of the type of pre-disinfectant used (Figure 26).

Because of the THM reductions noted by the use of pre-chlorine dioxide disinfection, an additional study was accomplished to determine the feasibility and benefits of using chlorine dioxide in Evansville's full-scale plant by extending the research effort with the pilot plant an additional four weeks. Although chlorine dioxide could be used as a pre-disinfectant, chlorine was desired as the post disinfectant because of the size of Evansville's distribution system and the need to maintain a sufficient disinfectant level throughout this system. Data generated from previous runs indicated that maintenance of a chlorine dioxide residual over an extended period of time was difficult.

The pilot plant GAC contactors were by-passed for the duration of this run in order to simulate the full-scale plant as close as possible. Chlorine dioxide was introduced into the raw water in sufficient quantities to maintain a slight residual through mixed media filtration (average addition of 1.1 mg/L

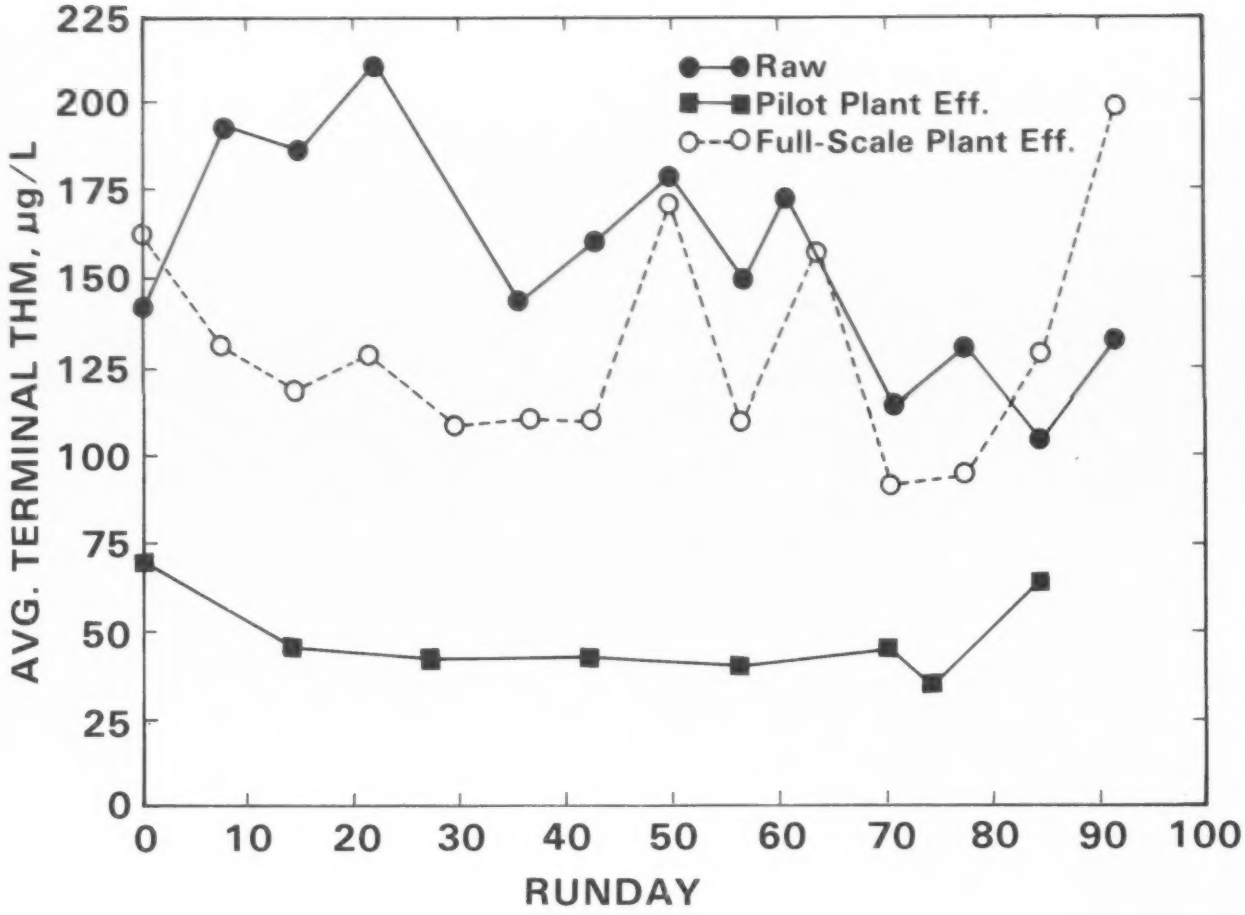

FIGURE 26. COMPARISON OF FULL-SCALE AND PILOT PLANT EFFULENT - AVG. TERM THM.

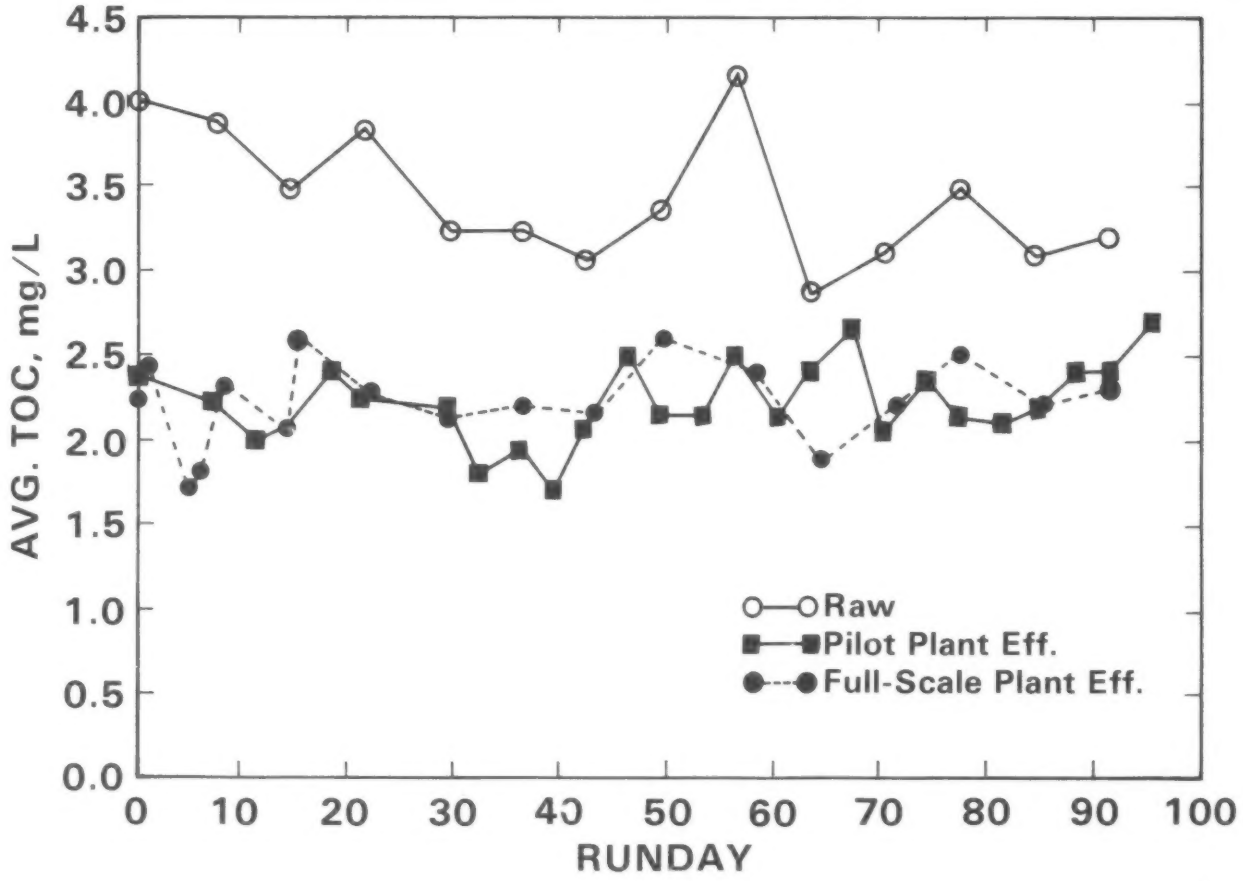

FIGURE 27. COMPARISON OF FULL-SCALE AND PILOT PLANT EFFLUENT - AVG. TOC.

and residual after filtration of 0.1 mg/L). Chlorine was introduced into the water prior to entering the pilot plant clearwell. The average residual concentration of chlorine in the clearwell was 2.1 mg/L. This concentration in the clearwell was representative of that being used in Evansville's treatment process.

As in previous runs, routine sampling for turbidity, pH, temperature, chlorine and chlorine dioxide residuals, total coliform, and standard plate counts were performed on both plants. In addition, instantaneous THMs were analyzed for the raw water, pilot plant filter effluent and clearwell, and the full-scale plant effluent. The instantaneous THM data again showed a reduction in the THMs by utilizing pre-chlorine dioxide disinfection as shown in Figure 27. No difference in the bacteriological quality of the two chlorinated plant effluents was noticed.

Additional Observations

Simulated Distribution

As previously mentioned, a water pipe connected to the pilot plant clearwell was used to simulate the drinking water retention time of Evansville's distribution system. During the course of the long-term phase, the only disinfection which occurred within this pipe originated from a ClO_2 residual present in the clearwell. As the project progressed, it became increasingly apparent that the data generated from this particular location was fluctuating excessively. The largest variations occurred with the standard plate counts and seemed to be relatively independent of the average ClO_2 residuals present. A routine flushing program was implemented in an attempt to control the high counts that were occurring in this simulated system, but this procedure failed to eliminate the wide variations in the standard plate count parameter. Although the total coliform counts remained at a desirable level, the data generated from this sampling point were not representative of the conditions that would exist in a large distribution system.

Tetrachloroethylene

In the short term studies, tetrachloroethylene concentrations appeared to increase in samples stored with chlorine as contrasted to samples stored with chlorine dioxide. This phenomenon was further evaluated in the long-term studies but no difference was noted (except on a sporatic basis) between the instantaneous samples containing chlorine dioxide and those stored with chlorine.

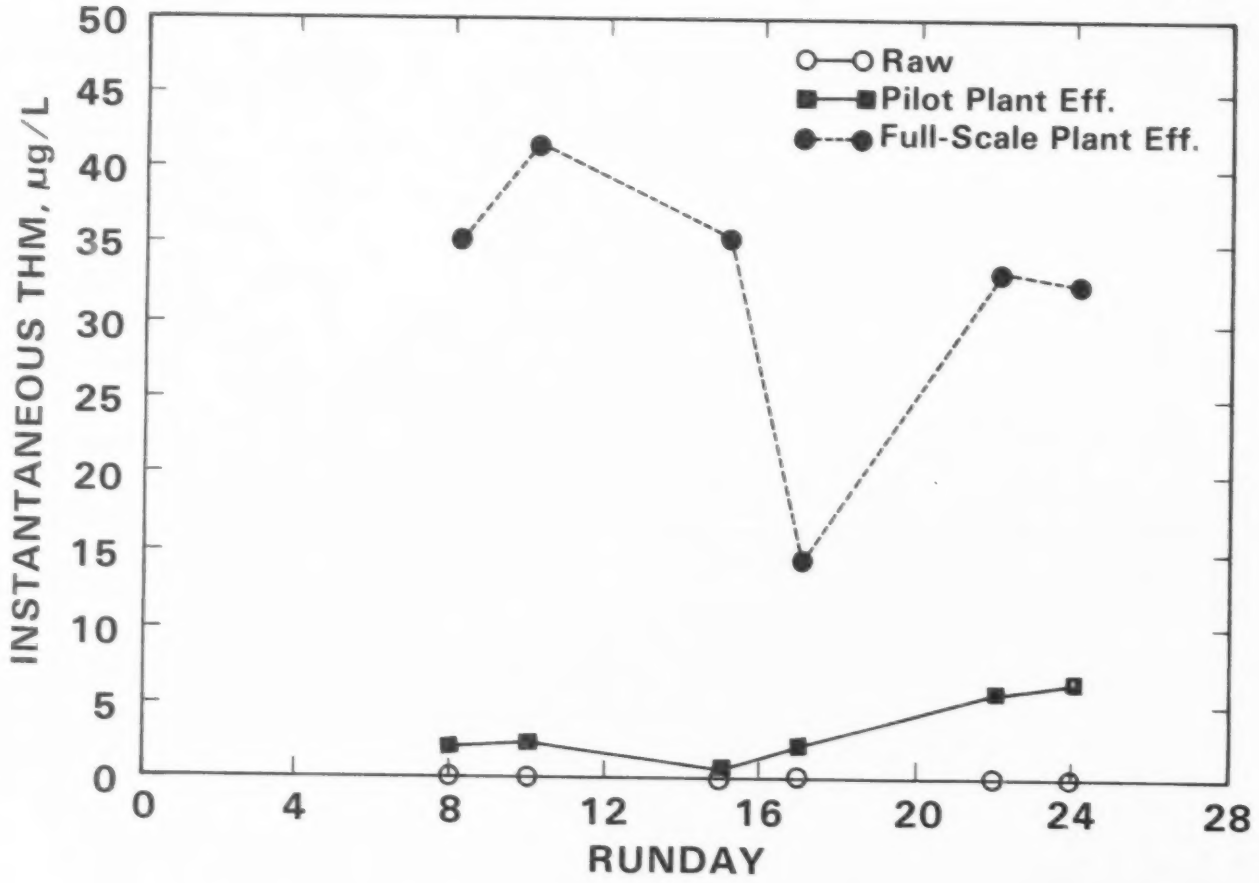

FIGURE 28. INSTANTANEOUS THM CONCENTRATIONS FOR PILOT PLANT AND FULL-SCALE PLANT (ClO_2 VS. Cl_2 DISINFECTION).

REFERENCES

1. Lykins, B.W. Jr., and DeMarco, J., "Pilot Plant Study on the Use of Chlorine Dioxide and Granular Activated Carbon", Presented at ACS National Meeting, Environmental Chemistry Division, Atlanta, GA, April 1, 1981.

2. LaMotte Chemical Products Co., "Instructions for Use of LaMotte-Palin DPD-FAS Titrimetric Unit, Chestertown, Maryland.

3. McGinnis, F. K., "Final Report on the First Regeneration of the Evansville, Indiana Carbon", Shirco, Inc., February, 1980.

4. McGinnis, F. K., "Final Report on the Second Regeneration of the Evansville, Indiana Carbon", Shirco Inc., May, 1980.

5. McGinnis, F. K., "Final Report on the Third Regeneration of the Evansville, Indiana Carbon", Shirco, Inc., January, 1981.

6. Phone conversation with Ramin Nur, County Sanitation District of Los Angeles County, Pomona, California 90607.

7. McGinnis, F. K. and Horwitz, G., "Effects of Thermal Regeneration on Activated Carbon Properties - A Critical Review of Traditional Physical and Chemical Tests", Presented at ACS National Meeting, Environmental Chemistry Division, Atlanta, GA, April 1, 1981.

8. Juhola, A. J., "Relationships of Iodine Adsorption and Pore Structure of Activated Carbon", Carbon, Vol. 13, pp 437-442, 1975.

9. DeMarco, J. and Brodtmann, N. V., Jr. "Prediction of Full-Scale Plant Performance from Pilot Columns", In: Proceedings - Symposium on Practical Application of Adsorption Techniques in Drinking Water Treatment, Reston, VA, April 30-May 2, 1979, USEPA, Washington, D. C.

10. Symons, J. M., Stevens, A. A., Clark, R. M., Geldreich, E. E., Love, O. T. Jr., and DeMarco, J., "Treatment Techniques for Controlling Trihalomethanes in Drinking Water", Research Report, Drinking Water Research Division, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, September, 1981.

11. Conversation with Leown Moore, Organic Control - Chemical Studies Section, Drinking Water Research Division, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio.

12. Reasoner, D. J. and Geldreich, E. E., "A New Medium for the Enumeration and Subculture of Bacteria from Potable Water", Presented at the 79th Annual Meeting of the American Society of Microbiology, May 4-8, 1979, Los Angeles, CA.

13. Love, O. T., Jr. and Symons, J. M., "Operational Aspects of Granular Activated Carbon Adsorption Treatment", Research Report, Drinking Water Research Division, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, July, 1978.

14. Palin, A. T. and Darrall, K. B., "A Modified DPD Titrimetric Procedure for Determination of Chlorine Dioxide and Chlorite in Water", J. Inst. Water Engrs. and Scientists, Vol. 33, pp. 467, 1979.

15. Palin, A. T., "Determining Chlorine Dioxide and Chlorite", Jour. AWWA, pg. 483, August, 1969.

16. Wagner, W. and Hull, C., "Synoptic Survey of Chlorite Determination and Synoptic Survey of Chlorate Determinations", Inorganic Titrimetric Analysis (Contemporary Methods), pp. 173-177, Marcell Dekker, Inc., New York, 1971.

17. Ramanauskas, E. and Sapragoniene, M., "Spectrophotometric Study of the Reactions of Chlorite Ion with Triphenylamine Dyes", Chemical Abstracts, Vol. 77, p. 614, 1972.

18. Sapragoniene, M. and Ramanauskas, E., "Spectrophotometric Determinaton of Chlorite by Basic Turquoise Blue and Methyl Violet", Chemical Abstracts, Vol. 76, p. 532, 1972.

19. Sapragoniene, M. and Ramanauskas, E., "Acid Triphenylamine Dyes as New Reagents for Determining Trace Amounts of Chlorite Ion", Chemical Abstracts, Vol. 76, p. 571, 1972.

20. Myhrstad, J. A. and Samdal, J. E., "Behavior and Determination of Chlorine Dioxide", JAWWA, pp. 205-208, August, 1968.

21. Miltner, R. J., "Measurement of Chlorine Dioxide and Related Products", Research Report, Drinking Water Research Division, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio, January, 1977.

22. Wheeler, G. L. and Lott, P. F., "A Rapid Microdetermination of Chlorine Dioxide in the Presence of Active Chlorine Compounds", Microchemical Journal, Vol. 23, pp. 160-164, 1978.

23. Granstrom, M. L. and Lee, G. F., "Generation and Use of Chlorine Dioxide in Water Treatment", JAWWA, pp. 1453-1466, November, 1958.

24. Masschelein, W. J., "The State of Art in the Use of Chlorine Dioxide and Ozone in the Treament of Water", Water SA, Vol. 6, No. 3, p. 116-129, July, 1980.

25. Masschelein, W. J., "The Use of Chlorine Dioxide in Drinking Water", Presented at the Conference on Oxidation Techniques in Drinking Water Treatment, Karlsruhe, Germany, September 11-13, 1978.

26. Augenstein, H. W., "Use of Chlorine Dioxide to Disinfect Water Supplies", JAWWA, pp. 716-717, December, 1974.

27. Brett, R. W. and Ridgeway, J. W., "Experiences with Chlorine Dioxide in Southern Water Authority and Water Research Centre", Journal of the Institution of Water Engineers and Scientists, Vol. 35, pp. 135-142, March, 1981.

28. Roberts, P. V., et al, "Chlorine Dioxide for Wastewater Disinfection: A Feasibility Evaluation", Final Report for EPA Grant No. R-805426, Wastewater Research Division, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, Ohio

29. Gall, R. J., "Chlorine Dioxide - An Overview of Its Preparation, Properties, and Use", Electrochemical Division, Hooker Chemicals and Plastics Corp., Niagara Falls, New York, no date.